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A Perturbation Theory of the Heisenberg Antiferromagnet

by

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UNIVERSITY OF CALIFORNIA - LOS ANGELES

A Perturbation Theory of the Heisenberg Antiferromagnet

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Physics

by

Donald Lynd Bullock

Final Examination for the Degree Doctor of Philosophy

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ABSTRACT OF THE DISSERTATION

A Perturbation Theory of the Heisenberg Antiferromagnet

by

Donald Lynd Bullock

University of California, Los Angeles, 1963

Assistant Professor David I. Paul, Chairman

The determination of some physical parameters of the ground state for the Heisenberg antiferromagnet is considered. This problem has been completely solved heretofore only in the cases of the energy and short range order parameters for the linear chain with spin one-half. In this dissertation, the problem of more general lattices and of arbitrary spin is considered, and the long range order parameter is treated in addition. The results are reported in terms of series expansions generated by means of a modified Rayleigh-Schrodinger perturbation theory, which is proposed and developed in this dissertation. The modification amounts to a process whereby the definition of the zero order Hamiltonian is changed through the prediction and inclusion of certain infinite classes of terms, whose first members appear in the original perturbation series. The final zero order Hamiltonian obtained is the

Ising model. Explicit expressions for the ground state parameters are given through fourth order for the linear chain, plane quadratic, and simple cubic lattices with arbitrary spin. The calculation is carried through to determine the energy series through six orders also for the linear chain with spin one-half. A comparison with experimental determinations of the long range order in real antiferromagnets is made. In addition, the problem of the first excited states is considered. A perturbation calculation similar to that performed for the ground state is carried out for the partition function of the Heisenberg antiferromagnet. The low temperature terms of this expansion are shown to be related to the energies of the ground state and first excited states. The calculation of the first excited state energies is carried out to second order. A complete analysis of the relationship of this perturbation method for the ground state and first excited states with the spin wave treatment of the same states is carried out.

I. INTRODUCTION

This dissertation concerns some physical properties of the ground state of the Heisenberg antiferromagnet. The approach is one of developing approximate series representations for various physical parameters by means of a modified Rayleigh-Schrodinger perturbation theory.

For classical and semi-classical treatments of antiferromagnetism, the problem of the ground state has been largely ignored, and the classical antiferromagnetic ground state, or Neel state, has been substituted for the true ground state. Interest in the true ground state remains, however, because the nature of the problem is such that its solution lies in the direction of an exact solution for the entire temperature range. Furthermore, there is the question of just how much similarity there is between the physical characteristics of the true ground state and the often substituted Neel state.

In Chapter II, the Heisenberg model is discussed, with emphasis on the problems inherent in treatments of the antiferromagnetic lowest energy eigenstate. Chapter III involves the derivation of an effective Hamiltonian, which is subsequently used in a modified perturbation theory. This modified perturbation theory is then proposed. The

modification amounts to a process whereby the definition of the zero order Hamiltonian is changed through the prediction and inclusion of certain infinite classes of terms whose first members appear in the original perturbation series. The final zero order Hamiltonian obtained in Chapter III is the Ising model. Perturbation series are then reported through the fourth order for the energy, short range, and long range order parameters for typical lattices of one, two, and three dimensions and arbitrary spin. In addition, an analysis of the relationship of these perturbation corrections to the corrections generated by the spin wave theory is carried out. In Chapter IV, the same treatment is applied to the first excited states of the Heisenberg antiferromagnet, along with a subsequent analysis of its relationship to the spin wave treatment of the same states.

The importance of this particular quantum mechanical treatment is that it is a new treatment of the Heisenberg antiferromagnet at low temperatures. Further, this new method is analyzed and then compared with the standard quantum mechanical approximation technique, i.e., the spin wave theory, thus giving additional insight into the problem.

II. THE HEISENBERG MODEL AND THE GROUND STATE PROBLEM

A. Discussion of the Model

Neel[1] was the first to propose, and extensively investigate, the antiferromagnetic state. The basis for his treatment of this state is the model Hamiltonian introduced by Heisenberg[2] in his first paper on the theory of ferromagnetism. This model continues to be the most common starting point for treatments of cooperative magnetic phenomena in both ferro- and antiferromagnetism, as well as in the intermediate case of ferrimagnetism.[3]

The Heisenberg model is useful in that it seems to be sufficiently representative of the physics of cooperative magnetism to predict with some consistency[3] the results of experiment. In spite of this success, however, there remain important theoretical problems with regard to the derivation and interpretation of the model. There is always the need to derive the model unambiguously from the full Hamiltonian expressed in terms of electron and nuclear coordinates, or to show that something quite like it exists.[4] Such a derivation would show clearly what constitute the limitations and omissions of the model.[5] There is also the need for the complete mathematical

solution of the model itself, i.e., determination of the eigenvalue spectrum and degeneracy scheme. The emphasis in this dissertation is with regard to a problem which lies in the latter area.

Complete descriptions of the eigenvalue spectrum and degeneracy scheme for the Heisenberg model do not exist, except for the treatment of the spin one-half coupled linear chain by Bethe.[6] Even for that case, determination of the eigenvalue spectrum and degeneracy is given only in principle. The set of coupled transcendental equations which result has been solved for the energy of the antiferromagnetic ground state[7] and of the antiferromagnetic first excited states,[8] as well as for some low-lying ferromagnetic states.[6] The great bulk of states which contribute to the thermodynamical properties at finite temperatures remains, however, uninvestigated. Progress with exact solutions of even the Ising model,[9] which is a considerably simplified abbreviation of the Heisenberg model, has so far failed of any exact three dimensional treatment. The present effort is directed toward the problem of the antiferromagnetic ground state for general spin and typical one, two, and three dimensional lattices from a perturbation theoretic point of view.

The mathematical statement of the Heisenberg model incorporating the nearest neighbor approximation is,

$$H = -2J \sum_{\langle jk \rangle} \vec{S}_j \cdot \vec{S}_k, \tag{1}$$

where J is the exchange integral, and the sum is carried out over the scalar product of all nearest neighbor pairs of spin angular momentum operators associated with a given lattice structure. Eq. (1) has both a classical and a quantum mechanical interpretation. The determinations of the lowest energy state when $\vec{S}_j$ and $\vec{S}_k$ are considered to be ordinary vectors, regardless of whether J is less than (antiferromagnetism) or greater than zero (ferromagnetism), is a trivial problem. For $J > 0$, all scalar products must be maximized, giving rise to a ground state configuration of perfect alignment which is fully determined except for a directional degeneracy[10] arising from the complete isotropy of (1). Ordinarily this directional degeneracy is resolved by introducing a finite anisotropy into Eq. (1). The directional degeneracy is removed completely for ferromagnetism by the introduction of an external magnetic field. For antiferromagnetism it is reduced to a double degeneracy by the internal crystalline anisotropy.

In the antiferromagnetic case, $J < 0$, the minimization of H results in the minimization of the individual scalar products only if the total lattice can be divided into two equivalent interlocking sublattices such that all nearest neighbors of a given sublattice point lie on the other sublattice. Again, this is fully determined except for

a directional degeneracy. (In Figure 1 are shown the classical ground state configurations for typical antiferromagnets.)

Quantum mechanics presents no special problem in the determination of the ground state for ferromagnetism. It is simply the quantum mechanical analog of the classical ground state, i.e., individual lattice point spin systems in states of maximum angular momentum along some common axis. For antiferromagnetism, however, the determination of the quantum mechanical ground state is a problem of considerable difficulty. In fact, only certain parameters of the antiferromagnetic ground state have been investigated.

For classical and semi-classical treatments of antiferromagnetism, the problem of the ground state has been largely ignored, and the classical antiferromagnetic ground state, or Neel state, has been substituted for the true ground state. Interest in the true ground state remains, however, because the nature of the problem is such that its solution lies in the direction of an exact solution for the entire model. Techniques which successfully treat the ground state may be applicable to certain other states, and eventually may be applicable to all other states. Furthermore, there is the question of just how much similarity there is between the physical characteristics of the true ground state and the often substituted Neel state.

B. Theoretical Treatments of the Ground State

The one exact treatment of an antiferromagnetic ground state has been previously mentioned.[6] This treatment of the spin one-half coupled linear chain provides a criterion for the comparison of all approximate treatments. Approximate methods which treat well the ground state of the linear chain are likely to treat well the ground state for other spins and lattices if the method is applicable.

During the past ten years there has been much activity related to the determination of the physical characteristics of the true ground state by means of approximation. The first quantum mechanical treatment for arbitrary spin systems in an interlocking sublattice structure was given by Anderson.[11] In it he applied what was qualitatively a spin wave approximation to Eq. (1). The results are valid for large values of the total spin of individual lattice point systems (all lattice point systems having a common total spin) and, when extrapolated to values of the spin of order unity, give physically interesting predictions of the sublattice magnetization (long range order). Of course, the ground state eigenvalues were also determined, but since they are not susceptible to experimental verification, their importance is relegated to the role of comparison with the eigenvalues determined by other methods. Anderson did point out, however, that in all cases treated his approximate eigenvalue lay within rigorously determined

limits[12] for the true eigenvalue--thus establishing that the method, at the very least, treats the energy adequately.

A special treatment of the short range order for the spin one-half coupled linear chain was considered by Hulthen.[7] The variational technique which he used was improved upon by Kasteleijn[13] and extended to an anisotropic Hamiltonian which is a function of a parameter, and has as its limiting cases the Heisenberg and Ising models. Kasteleijn also calculated the long range order for this case, and the results obtained in the Heisenberg limit were qualitatively the same as the predictions of the spin wave theory of Anderson. However, Orbach[14] was able to calculate the energy and short range order for this case as a function of the anisotropy without approximation, and his results are materially different from those of Kasteleijn. This cast serious doubt upon the reliability of the variational treatments as applied to the determination of antiferromagnetic ground state parameters.

Prior to Orbach's discovery, the variational treatment of Kasteleijn had been extended to other cases. Taketa and Nakamura[15] extended the Kasteleijn treatment, including the anisotropy parameter, to two and three dimensional lattices. Their results in the isotropic limit were in disagreement with those of Anderson for these

cases, since their long range order parameters exhibited a behavior as a function of the anisotropy which was similar to that of Kasteleijn's for the linear chain.

Marshall,[16] using the isotropic (Heisenberg) Hamiltonian and a combination of the variational method and the Bethe-Peirls approximation,[17] calculated the energy, short range, and long range order parameters for two and three dimensional spin one-half systems, obtaining predictions which were also in conflict with the spin wave theory. On the other hand, Kubo[18] used a combination of the variational method and the spin wave approximation itself to treat lattices of one, two, and three dimensions and arbitrary spin, obtaining results which were in agreement with the spin wave theory except in the case of one dimension. For the one dimensional lattice, Kubo predicted an ordered ground state, a result which is in contradiction to the spin wave theory.

C. Recent Perturbation Treatments of the Ground State

In the past few years, three new perturbation treatments of Eq. (1) for the ground state have been introduced. The original perturbation treatment of Eq. (1) consisted of a division into the spin wave Hamiltonian plus a perturbation. Walker[19] reports a perturbation treatment of the energy, short range order, and long range order of the spin one-half coupled linear chain through sixth order,

using the Ising model as a zero order Hamiltonian. For comparison with the exact treatments of the energy and short range order, he derives a series solution expressed in terms of the same parameter as was used in the perturbation treatment directly from the integral equations as given by Orbach.[14] The agreement between the two series is complete through sixth order.

The division of Eq. (1) used by Davis[20] to develop a "linked cluster" expansion for the energy, short range order, and long range order is

$$H_o = -2J \sum_{<jk>} [S_j^z S_k^z - (S - S_j^z)(S + S_k^z)] \qquad (2)$$

$$H_1 = -2J \sum_{<jk>} [(S - S_j^z)(S + S_k^z) + (1-a)(S_j^x S_k^x + S_j^y S_k^y)].$$

Although H_o does not retain as much of Eq. (1) as does the Ising model, it describes a system of "independent particles," for which Davis is able to prove the existence of a "linked cluster" expansion. Using this technique, he is able to report perturbation corrections through the seventh order in H_1 for all three ground state parameters. In order to improve convergence, he also reports contributions from higher orders, which he is able to predict on the basis of regularities evident in the first seven orders. He obtains energy eigenvalues comparable with those

obtained by other workers and predicts order in the ground state for the Heisenberg limit of Eq. (2) for all three dimensions.

The zero order Hamiltonian considered by Roth[21] is the long wavelength limit of a Fourier transform of Eq. (1), i.e.,

$$H_0 = -2J\gamma_0[S^x_{0_1} S^x_{0_2} + S^y_{0_1} S^y_{0_2} + S^z_{0_1} S^z_{0_2}] \qquad (3)$$

$$H_1 = -2J \sum_K{}' \gamma_K[S^x_{K_1} S^x_{-K_2} + S^y_{K_1} S^y_{-K_2} + S^z_{K_1} S^z_{-K_2}].$$

The prime on the summation symbol indicates the omission of the long wavelength term, K = 0. The transformed operators are of the form

$$S^x_{K_1} = \left(\frac{2}{N}\right)^{1/2} \sum_j \exp\ (iK\cdot j) S^x_j, \qquad (4)$$

$$S^x_{-K_2} = \left(\frac{2}{N}\right)^{1/2} \sum_k \exp\ (-iK\cdot k) S^x_k.$$

The sum over j represents a sum over lattice sites belonging to one of the sublattices, and the sum over k represents a sum over sites belonging to the other sublattice. N is the total number of lattice sites in the crystal, and

$$\gamma_K = \sum_{\delta} \exp\ (iK\cdot\delta) \qquad (5)$$

with δ representing the vector separation between nearest neighbors. The advantage of this particular division of Eq. (1) into zero order and perturbation parts is that H_0 is isotropic. The convergence properties of the series are similar to the Davis[20] series for the energy before the inclusion of the terms from orders higher than the seventh. No short range order or long range order series have been reported using Eq. (3).

In addition to the above three perturbation treatments of the ground state, Boon[22] has developed an energy series based on the Ising model as zero order Hamiltonian which is arbitrary in the spin and dimension of the lattice. His results, however, are different from the results obtained later in this dissertation for the general case. They differ with Walker[19] also for the linear chain.

Table I gives the qualitative results with regard to the prediction of a finite sublattice magnetization for all of the treatments mentioned previously which report such a quantity. The results are seen to be quite contradictory, but in general, the variational treatments predict zero sublattice magnetization and the perturbation treatments predict a finite sublattice magnetization. The explanations generally given for this situation are the following: (1) the perturbation treatments begin with

the perfectly ordered Neel state and then carry the perturbation through only a few orders in the calculation, resulting in a bias towards predicting sublattice magnetization in the ground state, and (2) the variational treatments reflect the existence of a statistically large number of low-lying states which exhibit zero sublattice magnetization. Thus the existence of a sublattice magnetization in the antiferromagnetic ground state seems to be unanswered in spite of the numerous attempts to determine it.

From an experimental point of view, real antiferromagnets do exhibit a sublattice magnetization at low temperatures.[23,24] If the Heisenberg model is to give a correct picture for antiferromagnetism, then it must predict a finite sublattice magnetization for, at the very least, the ground state region. If the Heisenberg model is assumed to be essentially correct for antiferromagnetism, then it must be concluded that the number of low-lying states exhibiting zero sublattice magnetization do not statistically outnumber those exhibiting a finite sublattice magnetization. This being the case, the predictions of the variational treatments cannot be explained away in manner previously suggested. Of course, if the Heisenberg model does not give the picture for a real antiferromagnet, then it may be true that the low-lying states exhibiting zero sublattices magnetization outnum-

ber those with finite sublattice magnetization for the model.

Recently, there have been some new speculations on the existence of a sublattice magnetization for the Heisenberg model antiferromagnetic ground state which affect the interpretation of both the perturbation and variational approaches. Pratt[25] has pointed out that, if the ground state is non-degenerate, the time reversal symmetry of the Hamiltonian of Eq. (1) requires the sublattice magnetization to be zero. In addition, the same arguments may be applied to anisotropic Hamiltonians of the form of Eq. (2). Karayianis, et al.,[26] have shown that the ground state of the spin one-half coupled linear chain is non-degenerate for arbitrary value of the anisotropy (except for the Ising limit), so that the arguments of Pratt certainly apply to this case. In the Ising limit, there is a degeneracy in the ground state consisting of the two time reversal symmetric Neel states for the linear chain which are shown in Figure 1. Each of these states alone exhibits perfect sublattice magnetization, but the correct linear combination of them which fits onto the ground state wave function near the Ising limit is the normalized sum of the two Neel states, which exhibits zero sublattice magnetization. This makes the prediction of zero sublattice magnetization for the anisotropically coupled linear chain with spin one-half consistent throughout the range of the anisotropy parameter.

In view of this development for the ground state of the spin one-half coupled linear chain, it is important to consider what effect a similar development for other cases may have on the interpretation of sublattice magnetization calculations, such as the one performed in this dissertation. Since a sublattice magnetization must be accepted as a property of all real antiferromagnets at very low temperatures, and since the Heisenberg model seems essentially correct for the discussion of many properties of real antiferromagnets, it will be assumed without further discussion that the time reversal symmetry argument is disqualified in some way for the purposes of this dissertation. This might come about through the degeneracy of the ground state for the important three dimensional cases, or through the destruction of the time reversal symmetry by some kind of non-time-reversal-symmetric interaction. Thus a finite sublattice magnetization will be assumed possible, and the Neel state will be chosen for a zero order wave function.

We now turn to the main purpose of this dissertation, which is to propose a new perturbation approach to the physical properties of the antiferromagnetic ground state.

III. PERTURBATION THEORY OF THE ANTIFERROMAGNETIC GROUND STATE

A. The Effective Hamiltonian

1. Division of the Hamiltonian

In this chaper we propose a new perturbation approach to the problem of the antiferromagnetic ground state. We generate a series for the energy which is general in the spin and valid for any interlocking sublattice system. The Ising model is taken to be the zero order approximation, and in this way our series differs from both the spin wave theory,[11] the linked cluster perturbation treatment,[20] and the diagram technique.[22] Such a zero order approximation affords a means of determining the ground state parameters without being subject to such criticisms as the inclusion of non-physical states and the omission of the dynamical interaction.[28] Also, the unconventional way in which we obtain the Ising model for zero order approximation affords a means of determining the sublattice magnetization directly from the energy series by means of the Feynman theorem.[29] This is not a property of an energy series based strictly on the Ising zero order approximation.

The method outlined below is most similar to the work

of Davis,[20] but it differs in two important respects. First, it does not require the use of a linked cluster criterion for the determination of physical contributions to the perturbation series. Second, it leads to the complete recovery of the Ising model as zero-order Hamiltonian through four orders of the perturbation for the general case, and six orders for the spin one-half coupled linear chain. This second difference is probably the more significant since it affords a basis upon which an instructive comparison with the spin wave treatment of the ground state is possible.

2. Discussion of the Anisotropy

We begin our perturbation treatment with the construction of an effective Hamiltonian to replace Eq. (1). We first write Eq. (1) in a slightly different form, i.e.*

$$H = 2J \sum_{<jk>} S_j^z S_k^z + J(1-a) \sum_{<jk>} (S_j^x S_k^x + S_j^y S_k^y). \qquad (6)$$

By introducing the parameter a and allowing this parameter to take on non-zero values, we are modifying

---

*Here we have written the Hamiltonian so that J is positive definite for antiferromagnetism, and thus J carries no implicit sign change for any expression involving J.

Eq. (1) to include the effects of anisotropy. In a physical sense, we are introducing a form of the anisotropic exchange interaction which was derived by Van Vleck[30] for exchange coupled spin one-half magnetic ions. This interaction takes the following form for arbitrary spin.

$$H_{int.} = \sum_{\mu\nu} C^{(jk)}_{\mu\nu} S^{\mu}_{j} S^{\nu}_{k}, \tag{7}$$

where j and k refer to different lattice sites, and μ and ν denote the three components of spin angular momentum. The $C^{(jk)}_{\mu\nu}$ may be determined from a second order perturbation calculation involving the spin-orbit coupling and wave function overlap between nearest neighbor ions. For $S = 1/2$, all $C^{(jk)}_{\mu\nu}$ with $\mu \neq \nu$ are identically zero, giving rise to a form which is comparable with the anisotropy introduced in Eq. (6). Even for cases in which $S \neq 1/2$, our form of the anisotropy is comparable with Eq. (7) provided the $C^{(jk)}_{\mu\nu}$ for $\mu \neq \nu$ are sufficiently small.

In a mathematical sense, the introduction of the parameter a allows Eq. (6) to represent either the Ising model, (a=1), or the Heisenberg model, (a=0). In addition, for a perturbation calculation based upon the Ising model as zero order approximation, the factor (1-a) serves as a perturbation parameter.

3. Transformation to Reciprocal Lattice Space

The commutation relations for spin operators attached to the various lattice points are

$$(S_j^z, S_k^+) = \delta_{jk} S_j^+, \tag{8}$$

$$(S_j^z, S_k^-) = -\delta_{jk} S_j^-,$$

and

$$(S_j^+, S_j^-) = 2\delta_{jk} S_j^z,$$

where we have introduced the usual relationship between spin components and the raising and lowering operators,

$$S^+ = S^x + iS^y, \tag{9}$$

$$S^- = S^x - iS^y.$$

Using these relationships and the transformation to reciprocal lattice space, i.e.,

$$\overrightarrow{S_{\lambda_1}} = (2/N)^{1/2} \sum_j \exp(i\lambda \cdot j) \overrightarrow{S_j} \tag{10}$$

and

$$\overrightarrow{S_{-\lambda_2}} = (2/N)^{1/2} \sum_k \exp(-i\lambda \cdot k) \overrightarrow{S_k},$$

where the summations over j and k represent summations over the lattice vectors of the two respective sublattices, we find for Eq. (6),

$$H = 2J\sum_{\lambda}\gamma_{\lambda}S^{z}_{\lambda_1}S^{z}_{-\lambda_2} + J(1-a)\sum_{\lambda}\gamma_{\lambda}(S^{+}_{\lambda_1}S^{-}_{-\lambda_2}+S^{-}_{\lambda_1}S^{+}_{-\lambda_2}), \quad (11)$$

where

$$\gamma_{\lambda} = \sum_{\delta} \exp\,(i\lambda\cdot\delta). \quad (12)$$

The vector δ represents the separation of nearest neighbor lattice sites. The commutation relations in reciprocal lattice space are

$$(S^{z}_{\lambda_n}, S^{+}_{\mu_m}) = (2/N)^{1/2}\delta_{nm}S^{+}_{\lambda_n+\mu_m}, \quad (13)$$

$$(S^{z}_{\lambda_n}, S^{-}_{\mu_m}) = -\,(2/N)^{1/2}\delta_{nm}S^{-}_{\lambda_n+\mu_m},$$

and

$$(S^{+}_{\lambda_n}, S^{-}_{\mu_m}) = 2(2/N)^{1/2}\delta_{nm}S^{z}_{\lambda_n+\mu_m}.$$

We define our Neel state ($|0\rangle$) to be

$$S^{+}_{\lambda_1}|0\rangle = 0, \quad (14)$$

$$S^z_{\lambda_1}|0> = (N/2)^{1/2} S\delta_{\lambda_0}|0>,$$

$$S^-_{\lambda_2}|0> = 0,$$

and

$$S^z_{\lambda_2}|0> = -(N/2)^{1/2} S\delta_{\lambda_0}|0>.$$

Thus 10> corresponds to a product of spin eigenfunctions, one for each lattice site, in which all eigenfunctions on the j sublattice (henceforth referred to as sublattice #1) have maximum z component of spin, and all those on the k sublattice (henceforth referred to as sublattice #2) have minimum z component of spin. This is perfect (i.e., classical) antiferromagnetic ordering.

Next, we express those states in which the z component of spin has been reduced by one on sublattice #1, and increased by one on sublattice #2. We do not need to investigate states in which the total z component of spin for the whole lattice is non-zero, since the Neel state has zero z component of spin and Eq. (11) conserves the total z component of spin. The states described above are of the form

$$S^-_j S^+_k|0>, \tag{15}$$

where j and k are arbitrary lattice sites in each of the two sublattices. In reciprocal lattice space Eq. (15) becomes

$$(2/N) \sum_{\lambda\mu} \exp\,[-i(\lambda\cdot j+\mu\cdot k)]S^-_{\lambda_1} S^+_{\lambda_2}|0>. \qquad (16)$$

The natural extension of Eq. (15) to other states with total z component of spin equal to zero, e.g., for a typical state

$$[(S^-_{j_1})(S^-_{j_2})\ldots(S^-_{j_n})] \times [(S^+_{k_1})(S^+_{k_2})\ldots(S^+_{k_n})]|0>, \qquad (17)$$

results in a reciprocal lattice wave function which is a linear combination of terms of the form

$$\Psi = \prod_{\lambda,\mu} B_1(a_\lambda)B_2(a_\mu)(S^-_{\lambda_1})^{a_\lambda}(S^+_{\mu_2})^{a_\mu}|0> \qquad (18)$$

where $\sum_\lambda a_\lambda = \sum_\mu a_\mu = n$. Thus we may take Ψ as representative of a typical wave function involving the reciprocal lattice spin operators and having total z component of spin equal to zero.

4. Construction and Physical Significance of the Effective Hamiltonian

We now define an effective Hamiltonian to replace Eq. (11). We begin by writing Eq. (11) as the sum of three

terms,

$$H_z = 2J\sum_{\lambda}\gamma_{\lambda}S^z_{\lambda_1}S^z_{-\lambda_2}, \tag{19}$$

$$H_U = J(1-a)\sum_{\lambda}\gamma_{\lambda}S^-_{\lambda_1}S^+_{-\lambda_2},$$

$$H_D = J(1-a)\sum_{\lambda}\gamma_{\lambda}S^+_{\lambda_1}S^-_{-\lambda_2}.$$

The second and third terms of Eq. (19) have the following physical significance: the second term decreases the z component of angular momentum on sublattice #1 by one unit, while simultaneously raising the z component of angular momentum on sublattice #2 by one unit. When applied to the Neel state described by Eq. (14), we may think of H_U as raising the Neel state to an excited state. This property of H_U is the reason for choosing the subscript U to denote this term of the Hamiltonian. The operator H_U raises a given state "up" from the point of view of the number of excitations present over the original Neel state. Correspondingly, the operator H_D lowers the number of excitations "down" from the number of excitations present. We shall leave H_U and H_D unchanged from their form in Eq. (19), and shall incorporate them directly into our new effective Hamiltonian. We derive this form by applying H_z to the typical wave function of Eq. (18). H_z may then be

commuted through all of the operators in ψ until it operates directly on the Neel state. The resulting extra terms all involve z component spin operators which are also commuted through all operators until they operate upon the Neel state. Since the Neel state is an eigenfunction of all z component spin operators, we may replace them with their eigenvalues to obtain

$$H_z\psi = [E_0 + \frac{\Delta}{2}(\sum_{\lambda} a_\lambda + \sum_{\mu} a_\mu)]\psi$$

$$- \frac{4J}{N}\sum_{\lambda'\mu'} a_{\lambda'} a_{\mu'} \sum_P \gamma_P (S^-_{\lambda'_1+\rho_1})(S^+_{-\mu'_2-\rho_2})(S^-_{\lambda'_1})^{-1}$$

$$(S^+_{-\mu'_2})^{-1}\psi, \tag{20}$$

where $E_0 = -2JS^2(N\gamma_0/2)$, $\Delta = 4JS\gamma_0$, and

$$(S^-_{\lambda'_1})^{-1}(S^-_{\lambda'_1}) = 1,$$

$$(S^+_{-\mu'_2})^{-1}(S^+_{-\mu'_2}) = 1.$$

Eq. (20) indicates that the Ising interaction may be expressed by the sum of two parts. The first part consists of a Hamiltonian which describes independent excitations above the Neel state, and the second part describes an interaction between these excitations. If we write the

Hamiltonian of the interaction as H_I, then our effective Hamiltonian takes the form[31]

$$H_{eff} = H_0 + H_I + H_U + H_D. \tag{21}$$

The operator form for H_0 is

$$H_0 = 2J(\tfrac{N}{2})^{1/2}\sum_{\lambda}\gamma_{\lambda}\delta_{\lambda_0}\left\{(\tfrac{N}{2})^{1/2}S^2 - S^z_{\lambda_1} + S^z_{-\lambda_2}\right\}, \tag{22}$$

but we may always represent Eq. (22) by its eigenvalues in the work that follows.

Having defined the effective Hamiltonian, we are now in a position to apply perturbation theory to Eq. (21).

B. The Application of a Modified Rayleigh-Schrodinger Perturbation Theory to the Neel State

1. The Modified Perturbation Method

We divide Eq. (21) into zero order and perturbation Hamiltonians,

$$H_0 = E_0 + \tfrac{\Delta}{2}\left(\sum_{\lambda} a_{\lambda} + \sum_{\mu} a_{\mu}\right), \tag{23}$$

and

$$H_1 = H_U + H_I + H_D \tag{24}$$

The ψ as defined constitute eigenfunctions of H_0.

We do not consider a particular choice of ψ to span the $(2S+1)^N$ dimensional spin space of interest, but only refer to the fact that such a choice exists.[31] Taking the Neel state for our zero order wave function, ψ_0, we have upon application to the Rayleigh-Schrodinger perturbation theory,

$$H_0\psi_0 = E_0\psi_0, \tag{25a}$$

$$H_0\psi_1 + H_1\psi_0 = E_0\psi_1 + E_1\psi_0, \tag{25b}$$

$$H_0\psi_2 + H_1\psi_1 = E_0\psi_2 + E_1\psi_1 + E_2\psi_0, \tag{25c}$$

etc.

The first order correction to the wave function, ψ_1, may be expressed as a sum of contributions involving different numbers of "independent" excitations, i.e.,

$$\begin{aligned}\psi_1 &= \psi_1^{(0)} + \psi_1^{(1)} + \psi_1^{(2)} + \ldots, \\ &= \sum_n \psi_1^{(n)},\end{aligned} \tag{26}$$

where

$$\psi_1^{(0)} = a_1^{(0)}|0\rangle,$$

$$\psi_1^{(1)} = \sum_{\rho\sigma} a_1^{\rho\sigma}(S_{\rho 1}^-)(S_{-\sigma 2}^+)|0\rangle,$$

etc. Here we have restricted ψ_1 to contributions of the form of Eq. (18) having an equal number of spin operators for each sublattice. Such contributions satisfy the eigenvalue equation,

$$S^z_{total}\psi_1^{(n)} = 0,$$

where S^z_{total} is the operator for the total z component of spin for the entire lattice, i.e., $S^z_{total} = \sum_j S^z_j + \sum_k S^z_k$. That only such contributions are necessary for the expansion of ψ_1 (or any higher order correction to the wave function ψ) follows from the two properties of H_1 and ψ_0, $S^z_{total}\psi_0 = 0$, and $(S^z_{total}, H_1) = 0$. In other words, the perturbation H_1 does not connect ψ_0 with any states having a different total z component of spin. We have previously discussed this property with respect to the total Hamiltonian, Eq. (11), but it is necessary here to specify it for the individual zero order and perturbation Hamiltonians.

Thus we have expressed ψ_1 in terms of a set $\psi_1^{(n)}$, where $\psi_1^{(n)}$ is a linear combination of states of the lattice wherein there are n spin operators $S^-_{\lambda_1}$ on sublattice #1, and n spin operators $S^+_{-\sigma_2}$ on sublattice #2. We notice that the $\psi_1^{(n)}$ are orthogonal in n. Further,

$$H_0\psi_1^{(n)} = (E_0 + n\Delta)\psi_1^{(n)}, \qquad (27)$$

and thus from Eq. (25b) we get

$$\Delta \sum_n \psi_1^{(n)} = (E_1 - H_U)\psi_0, \tag{28}$$

since $H_I\psi_0 = 0$, and $H_D\psi_0 = 0$. On the left of Eq. (28) are a set of contributions to ψ_1 arising from orthogonal subspaces of the original $(2S+1)^N$ dimensional spin space, and Eq. (28) must be satisfied separately in each of these subspaces. The components of H_1 have three important properties with respect to $\psi^{(n)}$,

$$H_U\psi^{(n)} = \phi^{(n+1)} \tag{29}$$

$$H_I\psi^{(n)} = \phi^{(n)},$$

and

$$H_D\psi^{(n)} = \phi^{(n-1)}.$$

H_U transforms a function $\psi^{(n)}$, defined entirely in the subspace n, into a function $\phi^{(n+1)}$, which is defined entirely in the subspace n + 1. H_I leaves unchanged the subspace in which $\psi^{(n)}$ is defined, and H_D transforms $\psi^{(n)}$ into a function $\phi^{(n-1)}$, which is entirely defined within the subspace n = 1.

In the n = 0 subspace we have from Eq. (28),

$$E_1\psi_0 = 0,$$

and therefore

$$E_1 = 0.$$

For n = 1 we have

$$\Delta\psi_1^{(1)} = -H_U\psi_0,$$

and therefore

$$\psi_1^{(1)} = -\frac{1}{\Delta}\cdot H_U\psi_0.$$

For $n \geq 2$ we find that $\psi_1^{(n)} = 0$, so the first order of the perturbation yields

$$E = E_0, \tag{30}$$

and

$$\psi = \psi_0 - \frac{1}{\Delta}H_U\psi_0,$$

since $\psi_1^{(0)} = 0$ in general.

Extending this procedure to higher order, and introducing the simplified notation

$$H_U \equiv U, \tag{31}$$

$$H_I \equiv I,$$

and

$$H_D \equiv D,$$

we find for the energy corrections through the sixth order

$$E_1 = 0, \tag{32}$$

$$E_2 = -\frac{1}{\Delta}\langle DU\rangle,$$

$$E_3 = 1/\Delta^2\langle DIU\rangle,$$

$$E_4 = 1/\Delta^3[\langle DU\rangle^2 - \langle DI^2U\rangle - \tfrac{1}{2}\langle D^2U^2\rangle],$$

$$E_5 = 1/\Delta^4[-3\langle DU\rangle\langle DIU\rangle + \langle DI^3U\rangle + \langle D^2UIU\rangle + \tfrac{1}{4}\langle D^2IU^2\rangle],$$

$$\begin{aligned} E_6 = 1/\Delta^5[&-2\langle DU\rangle^3 + 4\langle DU\rangle\langle DIU\rangle + 7/4\langle DU\rangle\langle D^2U^2\rangle \\ &+ 2\langle DIU\rangle^2 - \tfrac{1}{2}\langle DIDIU^2\rangle - \langle D^2UI^2U\rangle \\ &- \tfrac{1}{4}\langle D^2UDU^2\rangle - \langle DI^4U\rangle - \tfrac{1}{8}\langle D^2I^2U^2\rangle \\ &- \tfrac{1}{12}\langle D^3U^3\rangle - \tfrac{1}{2}\langle DIDUIU\rangle], \end{aligned}$$

where all expectation values are understood to be taken with respect to the Neel state.

2. The N-body Divergence Problem

When we calculate explicitly the value of the brackets, the brackets which contain a single D operator and a single U operator are found to be proportional to N, the total number of lattice sites in the crystal. Brackets with more than a single D and U are of a higher order of N. Thus, all terms of the E_n which are products of two or more brackets are at least of the order of N^2, and do not represent a physical contribution to the E_n. The argument given for this conclusion is that if $E_n \sim N^2$, then $E \sim N^2$, and the energy per lattice site, E/N, becomes unbounded as the number of lattice sites increases, i.e., $\lim_{N \to \infty} E/N \to \infty$. This is also true for higher powers of N. However, these non-physical terms are only apparent, for contained implicitly in other terms of the same order we find the negative of these terms.

Before we examine this cancellation for all six orders of Eq. (32), we investigate this cancellation in a related problem, i.e., that of a perturbation Hamiltonian consisting solely of the operators D and U. In other words, we assume $I \equiv 0$. Our energy terms are then

$$E_1' = 0, \tag{33}$$

$$E_2' = -\frac{1}{\Delta}\langle DU\rangle,$$

$$E_3' = 0,$$

$$E_4' = \frac{1}{\Delta^3}[\langle DU\rangle^2 - \frac{1}{2}\langle D^2U^2\rangle],$$

$$E_5' = 0,$$

and

$$E_6' = \frac{1}{\Delta^5}[-2\langle DU\rangle^2 + \frac{7}{4}\langle D^2U^2\rangle\langle DU\rangle - \frac{1}{4}\langle D^2UDU^2\rangle - \frac{1}{12}\langle D^3U^3\rangle].$$

We proceed to calculate these terms explicitly in order to show the cancellation of multiple bracket terms.

In E_2' we find that $\langle DU\rangle$ 2 $\langle Q\rangle$, where $Q = (D,U)$, the commutator of D and U. For $\langle Q\rangle$ we find

$$\langle Q\rangle = \frac{J^2(1-a)^2}{\gamma_0^2}(\frac{N\gamma_0}{2})4(S\gamma_0)^2. \tag{34}$$

In E_4' it is found that $\langle D^2U^2\rangle = 2\langle Q\rangle^2 + \langle F\rangle$, where $F = [D(Q,U)]$. A calculation of $\langle F\rangle$ yields

$$\langle F\rangle = \frac{J^4(1-a)^4}{\gamma_0^2}(\frac{N\gamma_0}{2})16(S\gamma_0)^2 \times [6(S\gamma_0)^2\frac{\gamma_0^{-1}}{\gamma_0^2} - 4(S\gamma_0) + 1]. \tag{35}$$

In E_6' we find that $\langle D^3U^3\rangle = 6\langle Q\rangle^3 + 9\langle Q\rangle\langle F\rangle + 2\langle R^+R\rangle + \langle V\rangle$, where $R = (Q,U)$ and $V = [D(F,U)]$. A calculation of

$\langle R^+R\rangle$ and $\langle V\rangle$ yields

$$\langle R^+R\rangle = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6(S\gamma_0)^2 \tag{36}$$

$$\times\ [4(S\gamma_0)^4\frac{(15\gamma_0^{\,2}-45\gamma_0+40)}{\gamma_0^{\,4}} - 48(S\gamma_0)^3\frac{\gamma_0-1}{\gamma_0^{\,2}}$$

$$+\ 4(S\gamma_0)^2\frac{(4\gamma_0^{\,2}+3\gamma_0-3)}{\gamma_0^{\,2}} - 8(S\gamma_0) + 1],$$

and

$$\langle V\rangle = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6(S\gamma_0)^2 \times [4(S\gamma_0)^4\frac{(15\gamma_0^{\,2}-45\gamma_0+40)}{\gamma_0^{\,4}}$$

$$- 120(S\gamma_0)^3\frac{\gamma_0-1}{\gamma_0^{\,2}} + 8(S\gamma_0)^2\frac{(5\gamma_0^{\,2}+36-3)}{\gamma_0^{\,2}} \tag{37}$$

$$-38(S\gamma_0) + 7].$$

Using Eqs. (34)-(37) in conjunction with Eq. (33), the energy correction through six orders is found to be

$$E_2' = -\frac{J(1-a)^2}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)(S\gamma_0), \tag{38}$$

$$E_4' = -\frac{J(1-a)^4}{8\gamma_0^2}\left(\frac{N\gamma_0}{2}\right)\frac{1}{(S\gamma_0)}$$

$$\times\ [6(S\gamma_0)^2\frac{\gamma_0-1}{\gamma_0^2} - 4(S\gamma_0) + 1],$$

and

$$E_6' = -\frac{J(1-A)^6}{64\gamma_0^2}\left(\frac{N\gamma_0}{2}\right)\frac{1}{(S\gamma_0)^3}$$

$$\times\ [8(S\gamma_0)^4\frac{(15\gamma_0^2-45\gamma_0+40)}{\gamma_0^4} - 120(S\gamma_0)^3\frac{\gamma_0-1}{\gamma_0^2}$$

$$+\ 8(S\gamma_0)^2\frac{5\gamma_0^2+6\gamma_0-6}{\gamma_0^2} - 29(S\gamma_0) + 4].$$

Each finite energy correction is strictly proportional to N.

Returning to the consideration of the total perturbation Hamiltonian, Eq. (24), we collect together all terms of Eq. (32) which are proportional to $(1-a)^2$,

$$E_2^{(1-a)^2} = -\frac{1}{\Delta}\langle DU\rangle, \tag{39}$$

$$E_3^{(1-a)^2} = \frac{1}{\Delta^2}\langle DIU\rangle,$$

$$E_4^{(1-a)^2} = \frac{1}{\Delta^3}\langle DI^2U\rangle,$$

$$E_5^{(1-a)^2} = \frac{1}{\Delta^4}\langle DI^3U\rangle,$$

and

$$E_6^{(1-a)^2} = -\frac{1}{\Delta^5}\langle DI^4U\rangle.$$

Since

$$IU|0\rangle = -2JU|0\rangle, \tag{40}$$

these energy corrections are manifestly proportional to N in view of Eq. (34).

For the contributions proportional to $(1-a)^4$, three of them have been calculated explicitly, i.e.,

$$E_4^{(1-a)^4} = \frac{1}{\Delta^3}\left\{\langle DU\rangle^2 - \frac{1}{2}\langle D^2U^2\rangle\right\}, \tag{41}$$

$$E_5^{(1-a)^4} = -\frac{1}{\Delta^4}\left\{3\langle DU\rangle\langle DIU\rangle - \langle D^2UIU\rangle - \frac{1}{4}\langle D^2IU^2\rangle\right\},$$

and

$$E_6^{(1-a)^4} = \frac{1}{\Delta^5}\left\{4\langle DU\rangle\langle DI^2U\rangle + 2\langle DIU\rangle^2 - \frac{1}{2}\langle DIDIU^2\rangle\right.$$

$$\left. - \langle D^2UI^2U\rangle - \frac{1}{8}\langle D^2I^2U^2\rangle - \frac{1}{2}\langle DIDUIU\rangle\right\}.$$

Using Eq. (40) and the similar relationships,

$$IU^2|0\rangle = -2J[2U^2|0\rangle + 2U_1U_{1'}|0\rangle], \tag{42}$$

where

$$U_1U_{1'}|0\rangle = \left(\frac{2}{N}\right)J^2(1-a)^2 \sum_{\lambda\sigma\mu} \gamma_\lambda \gamma_\sigma \gamma_\mu$$

$$\times\ (S^-_{\lambda_1+\mu_1})(S^+_{-\lambda_2})(S^-_{\sigma_1})(S^+_{-\sigma_2-\mu_2})|0\rangle, \tag{43}$$

and

$$I^2U^2|0\rangle = (-2J)^2\left\{4U^2|0\rangle + 10U_1U_{1'}|0\rangle + 2U_{12'}U_{1'2}|0\rangle\right\}, \tag{44}$$

where

$$U_{12'}U_{1'2}|0\rangle = \left(\frac{2}{N}\right)^2J^2(1-a)^2 \sum_{\lambda\sigma\mu\omega} \gamma_\lambda \gamma_\sigma \gamma_\mu \gamma_\omega \tag{45}$$

$$\times\ (S^-_{\lambda_1+\mu_1})(S^+_{-\lambda_2-\omega_2})(S^-_{\sigma_1+\omega_1})(S^+_{-\sigma_2-\mu_2})|0\rangle,$$

we find for $E_4^{(1-a)^4}$, $E_5^{(1-a)^4}$, and $E_6^{(1-a)^4}$,

$$E_4^{(1-a)^4} = -\frac{1}{\Delta^3}\langle F\rangle, \tag{46}$$

$$E_5^{(1-a)^4} = -\frac{2J}{\Delta^4}\left\{2\langle F\rangle + \frac{J^4(1-a)^4}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)16(S\gamma_0)^4\right\},$$

and

$$E_6^{(1-a)^4} = \frac{(-2J)^2}{\Delta^5}\left\{\frac{11}{2}\langle F\rangle\right.$$

$$\left. + \frac{24J^4(1-a)^4}{\gamma_0^2}\left(\frac{N\gamma_0}{2}\right)(S\gamma_0)^4\left(\frac{2\gamma_0^2+\gamma_0-1}{\gamma_0^2}\right)\right\}.$$

From Eq. (35), these energy corrections are also manifestly proportional to N.

3. <u>The Recovery of the Ising Model as Zero Order Hamiltonian</u>

Examination of Eq. (39) indicates that a very regular series is developing for the terms proportional to $(1-a)^2$. If we project this regularity to orders higher than the sixth, we obtain for the entire contribution to the energy which is proportional to $(1-a)^2$,

$$E^{(1-a)^2} = -\frac{1}{\Delta}\sum_{n=0}^{\infty}\left(-\frac{1}{\Delta}\right)^n\langle DI^nU\rangle = -\frac{\langle DU\rangle}{\Delta-2J}, \tag{47}$$

in view of Eq. (40). By predicting and including all terms proportional to $(1-a)^2$ in the energy correction, we are effectively recovering the Ising model as zero order Hamiltonian to second order in the perturbation.

In order to recover the Ising model through fourth order, we must be able to determine the regularities in the energy corrections which are proportional to $(1-a)^4$, which

we may represent by the expression

$$\sum_{n=4}^{\infty} E_n^{(1-a)^4}.$$

Assuming that terms proportional to powers of N greater than one are always cancelled out of our energy correction in each order n, as they were for n = 4, 5, and 6, the physically important part of the energy corrections is entirely contained in the single bracketed terms. These terms have the general form if proportional to $(1-a)^4$

$$\langle DI^p DI^m UI^q U\rangle;\ p,\ m,\ q \text{ integer.} \tag{48}$$

This is shown explicitly below. It is only necessary to reduce the terms of Eq. (48), i.e., remove contributions proportional to powers of N greater than one, to obtain the non-vanishing contribution to the perturbation correction. If we indicate a reduced term by a subscript R, then the entire contribution to the energy series which is proportional to $(1-a)^4$ may be written

$$E^{(1-a)^4} = -\frac{1}{2\Delta^3}\sum_{p,q,m=0}^{\infty}\left(-\frac{1}{\Delta}\right)^{p+q+m}\frac{1}{2^m}\langle DI^p DI^m UI^q U\rangle_R. \tag{49}$$

If we let m + p + q = 0, we get the single bracketed term in $E_4^{(1-a)^4}$. Letting p + m + q = 1 yields three single

bracketed terms, two of which are equivalent because of the Hermitian property of the brackets, i.e.,

$$\langle D^2UIU\rangle = \langle D^2UIU\rangle^+ = \langle U^+I^+U^+D^+D^+\rangle = \langle DIDU^2\rangle. \quad (50)$$

Thus p + q + m = 1 yields the single bracketed terms in $E_5^{(1-a)^4}$. Putting p + q + m = 2 yields the single bracketed terms in $E_6^{(1-a)^4}$, provided we use the Hermitian properties of the individual brackets.

With Eq. (40), together with the relationship

$$I^mU^2|0\rangle = (-2J)^m\Big\{2^mU^2|0\rangle + 2(3^m-2^m)U_1U_{1'}|0\rangle$$

$$+ (4^m-2\cdot 3^m+ 2^m)U_{12'}U_{1'2}|0\rangle\Big\}, \quad (51)$$

we find for $E^{(1-a)^4}$,

$$E^{(1-a)^4} = -\frac{1}{2(\Delta-2J)^3}\Big\{\langle F\rangle + \frac{2J}{\Delta-3J}\langle D^2U_1U_{1'}\rangle_R$$

$$+ \frac{(2J)^2}{2(\Delta-4J)(\Delta-3J)}\langle D^2U_{12'}U_{1'2}\rangle_R\Big\}. \quad (52)$$

A similar treatment of the terms in Eq. (32) which are proportional to $(1-a)^6$ may be undertaken. The expression equivalent to Eq. (49) for these terms, subject to the assumptions made in obtaining Eq. (49), is

$$E^{(1-a)^6} = -\frac{1}{12\Delta^5}\sum_{m,p,q,r,s=0}^{\infty}\left(-\frac{1}{\Delta}\right)^{m+p+q+r+s}\frac{1}{2^{r+s}}\frac{1}{3^m}$$

$$\times\ [\langle DI^p DI^r DI^m UI^s UI^q U\rangle_R$$

$$+\ 3^{m+1}\langle DI^p DI^r UI^m DI^s UI^q U\rangle_R]. \qquad (53)$$

In Appendix A we give the reduced form for Eq. (53), and perform the sums. The resulting expression for the general case is so unwieldy that it was determined that the additional correction obtained from calculating Eq. (53) was not worth the effort. It did, however, seem important to carry out the calculation of Eq. (53) for the spin one-half coupled linear chain, which is done in Appendix A. The numerical result is the same as that of a perturbation series developed by Walker[19] for this particular case, thus confirming our development of a perturbation series with the Ising model as zero order Hamiltonian.

C. The Perturbation Series for the Energy

1. The Second and Fourth Order Corrections for the General Cases

For arbitrary spin and for the linear chain, plane quadratic, and simple cubic lattices, the series expansion in powers of $(1-a)^2$ for the energy is

$$E = E_0[1 + C_2(1-a)^2 + C_4(1-a)^4 + C_6(1-a)^6 + \ldots] \qquad (54)$$

where

$$C_2 = \frac{1}{2(S\gamma_0) - 1},$$

$$C_4 = \frac{1}{16(S\gamma_0)[2(S\gamma_0) - 1]^3[4(S\gamma_0) - 3][(S\gamma_0) - 1]}$$

$$\times\ [192(S\gamma_0)^5\frac{\gamma_0 - 1}{\gamma_0^2} - 16(S\gamma_0)^4\frac{6\gamma_0^2 + 15\gamma_0 - 15}{\gamma_0^2}$$

$$+ 32(S\gamma_0)^3\frac{5\gamma_0^2 + 3\gamma_0 - 3}{\gamma_0^2} - 4(S\gamma_0)^2\frac{22\gamma_0^2 + 9\gamma_0 - 9}{\gamma_0^2}$$

$$+ 24(S\gamma_0) - 3].$$

In Table II are listed the values of C_2 and C_4 for the three lattices, where the spin is varied from $S = 1/2$ to $S = 2$. We also give the normalized (to the Ising ground state energy) energy for the isotropic case, $a = 0$. These are necessarily positive, and thus the larger the numerical result, the lower the corresponding ground state energy. For comparison we give the results obtained by the linked spin cluster method of Davis[20] for the equivalent of C_2 and C_4, and for the normalized energy through terms of the order of $(1-a)^4$ (Linked Cluster I in the table). We also repeat the final normalized energy reported for the linked spin cluster method, which includes part of the

contribution from terms of the order of $(1-a)^6$ (Linked Cluster II in the Table). Thus the difference between the final reported normalized energy and the normalized energy through terms of the order of $(1-a)^4$ for the linked spin cluster method (Linked Cluster II and I, respectively) lies with the partial calculation of C_6 performed by him.

For the linear chain with $S = 1/2$, we obtain the quite respectable value of 1.7500 for the normalized energy. The exact energy eigenvalue to five figures is 1.7726.[7] This may be compared with the spin wave ground state energy of 1.7268[11] and the linked spin cluster result of 1.7363. Upon investigating Table II, we find this work to yield lower eigenvalues than that of the linked spin cluster method for the cases in which the spin, S, and/or the dimensionality of the lattice is small. The partial calculation of C_4 in Linked Cluster II appears to be sufficient for the two dimensional lattice when $S \geq 3/2$, and for the three dimensional lattice when $S \geq 1$. For the one dimensional lattice, the partial calculation of C_4 does not seem to be adequate.

2. The Energy Series in the Spin Wave Theory as a Function of Ising Anisotropy

Turning to an examination of the spin wave theory of the antiferromagnetic ground state[11] and its first order correction given by Oguchi,[32] we determine its relationship to the present work. The spin wave theory has

proved to provide the most successful description of a Heisenberg antiferromagnet at temperatures $T \gg T_N$ (T_N = Neel temperature) short of an exact treatment of the model, and consequently one expects it to give an adequate description of the ground state. The spin wave Hamiltonian is obtained from Eq. (6) by replacing the angular momentum operators with equivalent operators, written in terms of the operators applicable to the problem of the linear harmonic oscillator, i.e.,

$$S_j^z = S - n_j, \tag{55}$$

$$S_j^+ = (2S)^{1/2}(1 - n_j/2S)^{1/=}a_j,$$

$$S_j^- = (2S)^{1/2}a_j^*(1 - n_j/2S)^{1/2},$$

$$S_k^z = - S + n_k,$$

$$S_k^+ = (2S)^{1/2}b_j^*(1 - n_k/2S)^{1/2},$$

$$S_k^- = (2S)^{1/2}(1 - n_k/2S)^{1/2}bj,$$

where

$$n_j = a_j^* a_j,$$

$$n_k = b_k^* b_k,$$

and

$$a_j a_j^* - a_j^* a_j = 1,$$

$$b_k b_k^* - b_k^* b_k = 1.$$

Substitution of the operators of Eq. (55) into Eq. (6) yields

$$H = -2JS^2\left(\frac{N\gamma_0}{2}\right) + 2JS\gamma_0\left(\sum_j n_j + \sum_k n_k\right) \tag{56}$$

$$+ 2JS(1-a)\sum_{\langle jk\rangle}(1 - n_j/2S)^{1/2} a_j (1 - n_k/2S)^{1/2} b_k$$

$$+ 2JS(1-a)\sum_{\langle jk\rangle} a_j^*(1 - n_j/2S)^{1/2} b_k^*(1 - n_k/2S)^{1/2}$$

$$- 2J\sum_{\langle jk\rangle} n_j n_k,$$

which, to order 1/S in the binomial expansion of the operators $(1 - n_j/2S)^{1/2}$, etc., equals

$$H = 2JS^2\left(\frac{N\gamma_0}{2}\right) + 2JS\gamma_0\left(\sum_j n_j + \sum_k n_k\right) \tag{57}$$

$$+ 2JS(1-a)\sum_{\langle jk\rangle}(a_j b_k + a_j^* b_k^*)$$

$$- \frac{1}{2}J(1-a)\left[\sum_{\langle jk\rangle}(n_j a_j b_k + a_j n_k b_k + a_j^* n_j b_k^* + a_j^* b_k^* n_k)\right]$$

$$- 2J \sum_{<jk>} n_j n_k .$$

The first three terms of Eq. (57) constitute the spin wave approximation, and the last two terms constitute the perturbation Hamiltonian considered by Oguchi. If the first term of Eq. (57) is considered to be of order unity, then the spin wave approximation is correct to order 1/S, and all of Eq. (57) is correct to order $1/S^2$.

We repeat the spin wave calculation, and the Oguchi correction, to the ground state because of the insertion of the anisotropy parameter (1-a) in Eq. (57). It will subsequently be shown that when a = 0, we obtain the results reported by Anderson and Oguchi. For the purpose of extracting the long range order parameter from our expression in later sections, we add to Eq. (57) the additional anisotropy

$$H_{anis} = g\beta H_A\left(\sum_j S_j^z - \sum_k S_k^z\right) = g\beta H_A\left[SN - \sum_j n_j - \sum_k n_k\right]. \tag{58}$$

Eq. (58) represents the anisotropy provided by an effective field which is directed oppositely on each sublattice, but it is inserted here simply because it allows the sublattice magnetization to be determined from the energy series by means of the Feynman theorem.[29]

The diagonalization of the spin wave Hamiltonian is accomplished by means of two successive canonical trans-

formations. The first transformation is to the operators belonging to the reciprocal lattice.

$$a_\lambda = (\tfrac{2}{N})^{1/2} \sum_j \exp\ (i\lambda\cdot j) a_j, \tag{59}$$

$$a_\lambda^* = (\tfrac{2}{N})^{1/2} \sum_j \exp\ (-i\lambda\cdot j) a_j^*,$$

$$b_\mu = (\tfrac{2}{N})^{1/2} \sum_k \exp\ (-i\mu\cdot k) b_k,$$

$$b_\mu^* = (\tfrac{2}{N})^{1/2} \sum_k \exp\ (i\mu\cdot k) b_k^*.$$

With these transformations, Eq. (57) plus Eq. (58) becomes

$$\begin{aligned} H = &- 2JS^2(\frac{N\gamma_0}{2}) + 2g\beta SH_A(\frac{N}{2}) \\ &+ 2JS\gamma_0(1 + \frac{g\beta H_A}{2JS\gamma_0})[\sum_\lambda (a_\lambda^* a_\lambda + b_\lambda^* b_\lambda)] \\ &+ 2JS(1-a) \sum_\lambda \gamma_\lambda (a_\lambda b_\lambda + a_\lambda^* b_\lambda^*) \\ &- 2J(1-a)(\tfrac{2}{N}) \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} [\delta(\lambda_1-\lambda_2-\lambda_3+\lambda_4)\gamma_{\lambda_4} a_{\lambda_1}^* a_{\lambda_2} a_{\lambda_3} b_{\lambda_4} \\ &+ \delta(-\lambda_1+\lambda_2-\lambda_3+\lambda_4)\gamma_{\lambda_1-\lambda_2-\lambda_4} b_{\lambda_1}^* b_{\lambda_2} a_{\lambda_3} b_{\lambda_4} \end{aligned} \tag{60}$$

$$+ \delta(-\lambda_1+\lambda_2-\lambda_3+\lambda_4)\gamma_{\lambda_2} a^*_{\lambda_1} b^*_{\lambda_2} a^*_{\lambda_3} a_{\lambda_4}$$

$$+ \delta(-\lambda_1+\lambda_2+\lambda_3-\lambda_4)\gamma_{\lambda_2+\lambda_3-\lambda_4} a^*_{\lambda_1} b^*_{\lambda_2} b^*_{\lambda_3} b_{\lambda_4}]$$

$$- 2J(\tfrac{2}{N}) \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \delta(\lambda_1-\lambda_2-\lambda_3+\lambda_4)\gamma_{\lambda_3-\lambda_4} a^*_{\lambda_1} a_{\lambda_2} b^*_{\lambda_3} b_{\lambda_4}.$$

Using the transformation to spin wave creation and destruction operators,

$$a_\lambda = \alpha_\lambda \cosh\theta \quad - \beta^*_\lambda \sinh\theta_\lambda, \tag{61}$$

$$b_\lambda = - \alpha^*_\lambda \sinh\theta \quad + \beta_\lambda \cosh \theta_\lambda,$$

$$a^*_\lambda = \alpha^*_\lambda \cosh\theta_\lambda \; - \beta_\lambda \sinh\theta_\lambda,$$

$$b^*_\lambda = - \alpha_\lambda \sinh\theta_\lambda + \beta^*_\lambda \cosh\theta,$$

with

$$t_{anh} 2\theta_\lambda = \frac{\gamma_\lambda(1-a)}{\gamma_0 D} \; ; \; D = 1 + \frac{g\beta H_A}{2JS\gamma_0} \; ,$$

we can diagonalize the spin wave Hamiltonian [the first four terms of Eq. (60)], resulting in

$$H_{SW} = 2JS^2(\frac{N\gamma_0}{2}) + 2g\beta H_A(\frac{N}{2})S \tag{62}$$

$$+ 2JS\gamma_0 \sum_\lambda [\alpha_\lambda^* \alpha_\lambda + \beta_\lambda^* \beta_\lambda][D^2 - \frac{\gamma_\lambda^2 (1-2)^2}{\gamma_0^2}]^{1/2}$$

$$- 2JS\gamma_0 \sum_\lambda \left\{D - [D^2 - \frac{\gamma_\lambda^2 (1-a)^2}{\gamma_0^2}]^{1/2}\right\}.$$

For the ground state, $\langle\alpha_\lambda^* \alpha\rangle = 0$ and $\langle\beta_\lambda^* \beta\rangle = 0$, and if also $H_A = 0$ we get for the energy of the ground state

$$E = - 2JS^2(\frac{N\gamma_0}{2}) - 2JS\gamma_0 \sum_\lambda \left\{1 - [1 - \frac{\gamma_\lambda^2 (1-a)^2}{\gamma_0^2}]^{1/2}\right\}, \tag{63}$$

which is Anderson's result when a = 0.

If we compute the first order perturbation correction to Eq. (63) using the remaining terms of Eq. (60) as a perturbation Hamiltonian, we obtain the equivalent of the ground state energy correction obtained by Oguchi, but with the insertion of the anisotropy parameter (1-a).

$$\Delta E = - 2JS^2(\frac{N\gamma_0}{2})(\frac{2}{NS})^2 \sum_{\lambda\mu} \frac{1}{4} \left\{ \left[\frac{D - \frac{\gamma_\mu^2 (1-2)^2}{\gamma_0^2}}{(D^2 - \frac{\gamma_\mu^2 (1-a)^2}{\gamma_0^2})^{1/2}} - 1 \right] \right. \tag{64}$$

$$\times\left[\frac{D - \frac{\gamma_\mu^2(1-a)^2}{\gamma_0^2}}{\left(D^2 - \frac{\gamma_\mu^2(1-a)^2}{\gamma_0^2}\right)^{1/2}} - 1\right]$$

$$+ a(2-a)(1-a)^2\frac{\gamma_\lambda^2\gamma_\mu^2}{\gamma_0^4}\left(D^2 - \frac{\gamma_\mu^2(1-a)^2}{\gamma_0^2}\right)^{1/2}$$

$$\left.\left(D^2 - \frac{\gamma_\lambda^2(1-a)^2}{\gamma_0^2}\right)^{-1/2}\right\},$$

which yields Oguchi's correction when $a = 0$.

Table III gives the eigenvalues $E + \Delta E$ for the cases investigated in Table II. In most cases, the spin wave theory plus the Oguchi correction yields eigenvalues which are lower than those yielded by our method. However, the correction for the linear chain with $S = 1/2$ badly overshoots the exact eigenvalue, while for the same lattice with $S = 1$ our method gives an eigenvalue which lies lower than that of the corrected spin wave theory. This oscillatory behavior of the corrected spin wave theory seems to be a property of the smallness of the spin, for a similar behavior may be seen in the plane quadradic and simple cubic lattices. Of course there are no exact values with which to compare in the two and three dimensional cases, and the oscillatory behavior is inferred from the behavior

of the corrected spin wave eigenvalues relative to those of our method.

3. Comparison of the Energy Series from the Spin Wave Theory with that of the Perturbation Theory

The relationship between the spin wave approach and the modified perturbation approach may be determined in a more elaborate manner than by a simple comparison of eigenvalues. This is possible because of the presence of the two expansion parameters, $1/S\gamma_0$ and $(1-a)^2$, common to the energy series of both methods. The entire contribution to the normalized energy eigenvalue of the antiferromagnetic ground state resulting from a continuation of either of the above methods may be expressed in the following general form,

$$E/E_0 = 1 + \sum_{n,m=1}^{\infty} a_{nm}(1-a)^{2n}(1/S\gamma_0)^m. \qquad (65)$$

Examination of Eq. (54) and Eq. (65) reveal the following relationships,

$$C_2 = \sum_{m=1}^{\infty} a_{1m}(1/S\gamma_0)^m, \qquad (66)$$

$$C_4 = \sum_{m=1}^{\infty} a_{2m}(1/S\gamma_0)^m,$$

and examination of Eq. (63), Eq. (64), and Eq. (65) yields

$$\text{Spin Wave Correction} = \frac{1}{S\gamma_0} \sum_{n=1}^{\infty} a_{n1}(1-a)^{2n}, \tag{67a}$$

$$\left.\begin{array}{l}\text{Oguchi Correction or}\\ \text{First Order Perturbation}\\ \text{Correction to the Spin}\\ \text{Wave Theory}\end{array}\right\} = \frac{1}{(S\gamma_0)^2} \sum_{n=1}^{\infty} a_{n2}(1-a)^{2n}. \tag{67b}$$

From Eq. (54), we can develop the first few terms of Eq. (66) explicitly, and from Eq. (63) and Eq. (64) we can develop the first few terms of Eqs. (67a,b) explicitly. The terms which are common to Eq. (66) and Eqs. (67a,b) are

$$a_{11} = 1/2, \tag{68}$$

$$a_{12} = 1/4,$$

$$a_{21} = \frac{(3\gamma_0-1)}{8\gamma_0^{\,2}},$$

$$a_{22} = -\frac{3(\gamma_0^2-4\gamma_0+4)}{16\gamma_0^{\,2}}.$$

Eq. (65) may be expressed in a tabular form, in which

the rows are labeled according to powers of $(1-a)^2$, and the columns by powers of $1/S\gamma_0$.

$$\frac{E}{E_0} = 1 + \begin{array}{c|c|c|c|c} & \frac{1}{S\gamma_0} & \frac{1}{(S\gamma_0)^2} & \frac{1}{(S\gamma_0)^3} & \frac{1}{(S\gamma_0)^4} \\ \hline (1-a)^2 & a_{11} & a_{12} & a_{13} & a_{14} \\ \hline (1-a)^4 & a_{21} & a_{22} & a_{22} & a_{24} \\ \hline (1-a)^6 & a_{31} & a_{32} & a_{33} & \\ \hline (1-a)^8 & a_{41} & a_{42} & & \\ \hline \end{array} \qquad (69)$$

Spin wave theory and its successive corrections correspond to adding the terms in the next column to the previous results. Beginning with the Ising model for a zero order Hamiltonian and computing succeeding orders of the perturbation corresponds to taking into account the terms of successive rows.

4. <u>A Hybrid Theory</u>

It now becomes possible to take advantage of all of the terms in Eq. (69) in both the first two columns and the first two rows to compute the ground state energy eigenvalue. This is done simply by adding together C_2, C_4, spin wave correction, and first order (Oguchi) correction. The twice counted terms, a_{11}, a_{12}, a_{21}, a_{22}, are then subtracted from the resulting sum. These results are

presented in Table III under the heading "Hybrid Method." The hybrid method yields an eigenvalue lying lower than either the corrected spin wave or the method of this dissertation, except for the spin one-half cases and the simple cubic spin two case.

The corrected spin wave theory may be expected to approach the exact eigenvalue for large spin and number of nearest neighbors. For the spin one-half cases, however, the apparently "better" (i.e., lower) eigenvalues produced by the corrected spin wave theory may be misleading. In the spin one-half linear chain, the lower eigenvalue given by the corrected spin wave theory must be raised by additional corrections, because it lies a great deal lower than the exact eigenvalue. In this particular case, the hybrid theory yields an eigenvalue which is less than $\frac{1}{2}\%$ in error. It seems likely that because of the behavior of the corrected spin wave eigenvalues which was pointed out at the end of Part (2), Section C of this chapter, the hybrid method gives the best eigenvalues, except as the spin gets relatively large.

We now turn to the consideration of the short and long range order parameters for the antiferromagnetic ground state.

D. Short and Long Range Order

1. The Feynman Theorem

There is a theorem due to Feynman,[29] which we now need in order to determine a perturbation series for the short and long range order parameters from the series for the energy. Briefly, the theorem is this: Given the eigenvalue equation

$$H(\lambda)\psi(\lambda) = U(\lambda)\psi(\lambda), \tag{70}$$

where $H(\lambda)$ is an operator expressed as a function of a parameter λ, then

$$\frac{\partial U(\lambda)}{\partial \lambda} = \int \psi^*(\lambda)\frac{H(\lambda)}{\partial \lambda}\psi(\lambda)\,dv. \tag{71}$$

For a proof of Eq. (71), the reader is referred to the article by Feynman.[29]

2. The Short Range Order in the Modified Perturbation Theory

Once the short range order parameter has been defined, the Feynman theorem may be used to generate the corresponding series from the energy series. However, it is necessary that the Hamiltonian be expressed as an explicit function of the short range order operator. The natural definition of the short range order operator is one which measures local spin correlation along some pre-

ferred axis, i.e.,

$$\eta_{op} = \frac{1}{S^2(\frac{N\gamma_0}{2})} \sum_{<jk>} S_j^z S_k^z. \tag{72}$$

η_{op} is the average spin correlation along the axis of anisotropy between spin systems on neighboring lattic sites. It is normalized so that for perfect ferromagnetic ordering, $<\eta_{op}> = 1$, for a system of completely independent spin systems, $<\eta_{op}> = 0$, and for perfect antiferromagnetic ordering, $<\eta_{op}> = -1$.

In terms of the Hamiltonian of Eq. (6), and thus also of Eq. (21), the short range order operator takes the form

$$\eta_{op} = \frac{1}{2JS^2(\frac{N\gamma_0}{2})}[1 + (1-a)\frac{\partial}{\partial a}]H. \tag{73}$$

Application of the Feynman theorem to Eq. (54) then yields

$$\eta = <\eta_{op}>_{\text{true ground state}} \tag{74}$$

$$= \frac{1}{2JS^2(\frac{N\gamma_0}{2})}[1 + (1-a)\frac{\partial}{\partial a}]\Big\{E_0[1 + C_2(1-a)^2$$

$$+ C_4(1-a)^4 + \ldots]\Big\}$$

$$= -1 + C_2(1-a)^2 + 3C_4(1-a)^4 + 5C_6(1-a)^6 + \ldots \quad .$$

Values of η in the isotropic limit (a=0), determined from Eq. (74), are given in Table IV. It is interesting to compare the approximate value of η, determined from Eq. (74), with the exact value of η in the isotropic limit, determined by Orbach,[14] for the spin one-half coupled linear chain. These are, respectively, $\eta = -0.7500$ and $\eta = -0.5909$. Thus, Eq. (74) does not represent the short range order with nearly the accuracy with which Eq. (54) represents the energy to this order in the perturbation. In Appendix A we determine C_6 to be zero for the spin one-half coupled linear chain, so that the value of η is not further modified until the eighth order of the perturbation. In Section E of this chapter, we will discuss further the properties of the short range order series for this particular case in conjunction with a discussion on the convergence properties of the energy, short range order, and long range order series for the general case.

3. The Short Range Order in the Corrected Spin Wave Theory

Application of Eq. (73) to the spin wave perturbation expansion of the energy, Eq. (63) plus Eq. (64), yields the short range order as determined by the corrected spin wave theory,

$$\eta = -1 + G_1 \frac{1}{S\gamma_0} + G_2\left(\frac{1}{S\gamma_0}\right)^2 + \ldots, \qquad (75)$$

where

$$G_1 = \gamma_0(\tfrac{2}{N})\sum_{\lambda}[(1-\frac{\gamma_\lambda^2}{\gamma_0^2}(1-a)^2)^{1/2} - 1],$$

$$G_2 = \gamma_0^2(\tfrac{2}{N})^2\sum_{\lambda\mu}\tfrac{1}{4}\Big\{[1 - (1 - \frac{\gamma_\lambda^2}{\gamma_0^2}(1-a)^2)^{1/2}]$$

$$\times [1 - (1 - \frac{\gamma_\mu^2}{\gamma_0^2}(1-a)^2)^{1/2}$$

$$- 2\frac{\gamma_\mu^2}{\gamma_0^2}(1-a)^2(1 - \frac{\gamma_\mu^2}{\gamma_0^2}(1-a)^2)^{-1/2}]$$

$$+ [(1-a)^2 - 3(1-a)^4][\frac{\gamma_\lambda^2}{\gamma_0^2}(1 - \frac{\gamma_\lambda^2}{\gamma_0^2}(1-a)^2)^{-1/2}]$$

$$[\frac{\gamma_\mu^2}{\gamma_0^2}(1 - \frac{\gamma_\mu^2}{\gamma_0^2}(1-a)^2)^{-1/2}] + 2[(1-a)^4 - (1-a)^6]$$

$$[\frac{\gamma_\lambda^2}{\gamma_0^2}(1 - \frac{\gamma_\lambda^2}{\gamma_0^2}(1-a)^2)^{-1/2}][\frac{\gamma_\mu^4}{\gamma_0^4}(1 - \frac{\gamma_\mu^2}{\gamma_0^2}(1-a)^2)^{-3/2}].$$

Values of η in the isotropic limit ($a = 0$), determined from Eq. (75) through G_2, are given in Table IV. However, no values are given for η in this approximation for the linear chain. This is because Eq. (75) is indeterminate for the one dimensional lattice. Both G_1 and G_2 are not finite for

this case, and thus this indeterminacy is independent of the spin. This behavior is definitely a property of the approximation, and not of the short range order parameter, since from Orbach's work[14] we know the short range order in the isotropic limit of the spin one-half coupled linear chain to be finite. We will find this behavior to be true also of the long range order for this lattice, when it is determined by means of the spin wave approximation. It is most likely due to the convergence properties of the series for these cases, i.e., when the terms in the series for the short and long range order are expressed in a form similar to that of Eq. (69) for the energy, convergence depends upon the order in which the terms are added up. If they are added up by rows (modified perturbation theory), convergence is evident, and if they are added up by columns (spin wave approximation), the series diverges.

In Table IV, we also include the short range order parameter as determined by the hybrid method of Section 5, Part (4) of this chapter.

4. Comparison of the Methods for the Determination of the Short Range Order

In view of the fact that the corrected spin wave theory is inadequate for the determination of the short range order of the only case for which the exact value is known, no absolute comparison of the methods is possible at present. Since the spin wave approximation represents

an expansion in powers of $1/S\gamma_0$, one expects it to be the best method when the spin and dimensionality of the lattice are large. However, as has already been pointed out, the short range order series diverges for the linear chain no matter how small the expansion parameter, and thus one cannot fully depend upon this criterion. We conclude that, for the short range order parameter, the modified perturbation theory gives the more meaningful prediction. This conclusion will be borne out in the discussion of the relative convergence of the series generated by the two methods which appears in Section E of this chapter.

5. <u>The Long Range Order in the Modified Perturbation Theory</u>

The choice of an operator to represent the long range order is restricted here by the conditions necessary for the application of the Feynman theorem. The natural extension of the operator which was used to represent the short range order would be one which measured the spin correlation along the axis of anisotropy, i.e.,

$$\rho_{op} = \lim_{\delta\to\infty} \frac{1}{S^2} S_j^z S_{j+\delta}^z , \tag{76}$$

or one which measures the general spin correlation,

$$\rho_{op} = \lim_{\delta\to\infty} \frac{1}{S(S+1)} \vec{S}_j \cdot \vec{S}_{j+\delta} . \tag{77}$$

The correlation is measured between spin systems which lie at large distances from each other, hence the concept of long range order. When a wave function is available, such definitions of the long range order operator as Eqs. (76-77) are possible,[33] but when use is made of the Feynman theorem, the condition that the Hamiltonian must be an explicit function of the long range order operator prevents the adoption of either Eq. (76) or Eq. (77). Consequently, we are constrained to use the concept of the sublattice magnetization, which bears some relationship to Eq. (76).

The sublattice magnetization operator may be expressed as follows:

$$\rho_{op} = \frac{1}{S(N/2)} \sum_j S_j^z \tag{78}$$

$$= 1 - \frac{1}{S(N/2)} \sum_j (S - S_j^z)$$

$$= 1 - \frac{1}{S(N/2)} \sum_\lambda a_\lambda$$

Thus, for perfect order, $\langle\rho\rangle = \pm 1$, depending upon the direction in which the sublattice is magnetized. For complete disorder, $\langle\rho\rangle = 0$. The concepts of order and disorder used in conjunction with Eq. (78) are not identical with those used with Eq. (76). The correlation between

spins at large distances can be such as to yield zero for the expectation value of Eq. (78), while yielding a finite value for the expectation value of Eq. (76). In other words, the spins at individual lattice sites may be changing with time in such a way as to wash out the average z component of spin, and yet be in step with the time variation of each other so that the average product is non-zero. If, however, the sublattice magnetization is finite, then the average z component of spin at individual lattice sites is not zero, and the spins are "pinned down" to point mainly in the z direction. In this case, Eq. (78) bears the following approximate relationship to Eq. (76),

$$
\begin{aligned}
\langle \rho \rangle_{\text{Eq.}(76)} &= \lim_{\delta \to \infty} \langle S_j^z S_{j+\delta}^z \rangle \qquad (79) \\
&\cong \lim_{\delta \to \infty} \langle S_j^z \rangle \langle S_{j+\delta}^z \rangle \\
&\cong \langle S_j^z \rangle^2 \\
&\cong \frac{1}{[S(\frac{N}{2})]^2} \langle \sum_j S_j^z \rangle^2 \\
&= \langle \rho \rangle^2_{\text{Eq.}(78)} .
\end{aligned}
$$

We will use this relationship later, when we compare values of ρ with η.

In order to apply the Feynman theorem, it is necessary to express the effective Hamiltonian, Eq. (21), as an explicit function of Eq. (78). We repeat Eq. (21), with H_0 replaced by its eigenvalues with respect to the set of states described in Eq. (18),

$$H_{eff} = E_0 + \frac{\Delta}{2}\left(\sum_{\lambda} a_{\lambda} + \sum_{\mu} a_{\mu}\right) + H_U + H_I + H_D \qquad (80)$$

with $\sum_{\lambda} a_{\lambda} = \sum_{\mu} a_{\mu}$. Thus $\sum_{\lambda} a_{\lambda} + \sum_{\mu} a_{\mu} = 2\sum_{\lambda} a_{\lambda}$, and

$$\sum_{\lambda} a_{\lambda} = \frac{\partial}{\partial\Delta} H_{eff}. \qquad (81)$$

The Feynman theorem then yields

$$\rho = \langle \rho_{op} \rangle_{\text{true ground state}} \qquad (82)$$

$$= 1 - \frac{\Delta}{4JS^2\left(\frac{N\gamma_0}{2}\right)} \frac{\partial}{\partial\Delta}\left\{E_0[1 + C_2(1-a)^2 + C_4(1-a)^4 + \ldots]\right\}$$

$$= 1 - D_2(1-a)^2 - D_4(1-a)^4 - \ldots,$$

where

$$D_2 = \frac{\langle DU \rangle}{4JS^2\left(\frac{N\gamma_0}{2}\right)} \frac{\Delta}{(\Delta-2J)^2} \qquad (83)$$

$$= \frac{(S\gamma_0)}{(2S\gamma_0-1)^2},$$

and, for $S\gamma_0 = 1$ (linear chain with spin one-half),

$$D_4 = \frac{\Delta}{8JS^2(\frac{N\gamma_0}{2})(\Delta-2J)^4}\left\{3\langle F\rangle + \frac{2(4\Delta-11J)J}{(\Delta-3J)^2}\langle D^2U_1U_{1'}\rangle\right\} \tag{84}$$

$$= \frac{S\gamma_0}{2(4S\gamma_0-3)^2(2S\gamma_0-1)^4}\left\{288(S\gamma_0)^4\frac{\gamma_0-1}{\gamma_0^2}\right.$$

$$-16(S\gamma_0)^3\,\frac{8\gamma_0^2+15\gamma_0-15}{\gamma_0^2}$$

$$+\,2(S\gamma_0)^2\,\frac{82\gamma_0^2+15\gamma_0-15}{\gamma_0^2}$$

$$\left.-\,60(S\gamma_0)+5\right\},$$

and, for $S\gamma_0 \neq 1$ (all other cases),

$$D_4 = \frac{\Delta}{8JS^2(\frac{N\gamma_0}{2})(\Delta-2J)^4}\left\{3\langle F\rangle + \frac{2J(4\Delta-11J)}{(\Delta-3J)^2}\langle D^2U_1U_{1'}\rangle\right. \tag{85}$$

$$\left.+\,\frac{2J^2(5\Delta^2-32J\Delta+50J^2)}{(\Delta-3J)^2(\Delta-4J)^2}\langle D^2U_{12'}U_{1'2}\rangle\right\}$$

$$= \frac{(S\gamma_0)}{8(2S\gamma_0-1)^4(4S\gamma_0-3)^2(S\gamma_0-1)^2}\left\{1152(S\gamma_0)^6\frac{\gamma_0-1}{\gamma_0^2}\right.$$

$$- 64(S\gamma_0)^5 \frac{8\gamma_0^2 + 51\gamma_0 - 51}{\gamma_0^2}$$

$$+ 8(S\gamma_0)^4 \frac{210\gamma_0^2 + 459\gamma_0 - 459}{\gamma_0^2}$$

$$- 16(S\gamma_0)^3 \frac{139\gamma_0^2 + 123\gamma_0 - 123}{\gamma_0^2}$$

$$+ 12(S\gamma_0)^2 \frac{121\gamma_0^2 + 35\gamma_0 - 35}{\gamma_0^2} - 444(S\gamma_0) + 45\Big\}.$$

The difference in the forms of D_4 for $S\gamma_0 = 1$ and $S\gamma_0 \neq 1$ arises from the fact that in Eq. (52) $\langle D^2 U_{12'} U_{1'2} \rangle_R = 0$ for $S\gamma_0 = 1$, and $\langle D^2 U_{12'} U_{1'2} \rangle_R$ is finite for $S\gamma_0 \neq 1$.

6. <u>The Long Range Order in the Corrected Spin Wave Theory</u>

Turning again to the corrected spin wave theory, we determine the expectation value for the long range order operator, Eq. (78). In view of Eq. (58) and the Hamiltonian, Eq. (60), application of the Feynman theorem yields

$$\rho = \frac{1}{g\beta NS} \frac{\partial E}{\partial H_A}, \tag{86}$$

where E is the sum of Eqs. (63) and (64). The series for ρ is then

$$\rho = 1 - K_1 \frac{1}{S\gamma_0} - K_2 \frac{1}{(S\gamma_0)^2} - \ldots, \qquad (87)$$

where

$$K_1 = \frac{\gamma_0}{2}\left(\frac{2}{N}\right)\sum_{\lambda} \left[\left(1 - \frac{\gamma_\lambda^2}{\gamma_0^2}(1-a)^2\right)^{-1/2} - 1\right],$$

$$K_2 = \gamma_0^2\left(\frac{2}{N}\right)^2 \sum_{\lambda\mu} \left[(1-a)^2 - (1-a)^4\right]$$

$$\times \frac{1}{4}\left\{\frac{\gamma_\lambda^2\gamma_\mu^2}{\gamma_0^4}\left(1 - \frac{\gamma_\mu^2(1-a)^2}{\gamma_0^2}\right)^{-1/2}\left(1 - \frac{\gamma_\lambda^2(1-a)^2}{\gamma_0^2}\right)^{-3/2}\right\}.$$

For a = 0, K_1 is the spin wave correction to the normalized sublattice magnetization (i.e., our long range order parameter), and $K_2 = 0$, consistent with the result of Oguchi.[32]

7. Comparison of the Methods for the Determination of the Long Range Order

In Table V are given the values of D_2 and D_4 for the cases investigated previously. In Table VI are given the values of ρ for the isotropic case (a=0) for the same cases, listed under the heading "this work." Also given in Table VI are the values of ρ predicted by the corrected

spin wave theory and the hybrid method of Part (4), Section C of this chapter. No values of ρ appear for the latter two methods as applied to the linear chain, for reasons similar to those given for the omission in Table IV with respect to the determination of η [cf. Part (3), Section D of this chapter]. This omission will be discussed further in Section E.

The total sublattice magnetization, determined by either the modified perturbation theory or the corrected spin wave theory, may be expressed in a form similar to that in which the energy was expressed in Eq. (69), i.e.,

$$\rho = 1 - \begin{array}{c|c|c|c|} & \frac{1}{S\gamma_0} & \frac{1}{(S\gamma_0)^2} & \frac{1}{(S\gamma_0)^3} \\ \hline (1-a)^2 & d_{11} & d_{12} & d_{13} \\ \hline (1-a)^4 & d_{21} & d_{22} & d_{23} \\ \hline (1-a)^6 & d_{31} & d_{32} & \\ \hline \end{array} \tag{88}$$

The terms common to D_2, D_4, K_1, and K_2 are

$$d_{11} = \frac{1}{4}, \tag{89}$$

$$d_{12} = \frac{1}{4},$$

$$d_{21} = \frac{9}{16}\,\frac{\gamma_0 - 1}{\gamma_0^{\,2}},$$

$$d_{22} = -\frac{8\gamma_0^{\,2} - 48\,\gamma_0 + 48}{32\gamma_0^{\,2}}$$

which are determined from Eq. (83) and either Eq. (84) or Eq. (85), or alternatively from Eq. (87).

In order to determine the power of the spin wave approach versus the modified perturbation theory, we also include in Table VI, under the heading of "overlap," the contribution to ρ which arises solely from the four terms common to both methods, i.e.,

$$\text{overlap} = 1 - (d_{11}+d_{21})\frac{1}{S\gamma_0} - (d_{12}+d_{22})\frac{1}{(S\gamma_0)^2} \,. \tag{90}$$

It is apparent from Table VI that the overlap between the two methods constitutes far and away the largest contribution to the divergence of the sublattice magnetization from unity in the three dimensional cases. Not quite so strong a statement may be made for the two dimensional cases, and the modified perturbation method seems to be the only satisfactory approach for the one dimensional lattice. Thus, both methods are roughly comparable in three dimensions, and one could not hope to obtain very different results for the ground state sublattice magnetization by choosing one method in preference to the other.

The long range order parameter is larger in absolute magnitude than the short range order parameter in almost

all of the cases of the Tables IV and VI. At first glance, it might be thought that η should at all times be larger than ρ, because of the comparative distances over which correlation is being measured. The fact that this is not reflected in the computed values may be attributed to the way in which our long range order parameter has been defined. Our definition, Eq. (78), which is the only one available to our theory, is not the proper analog of our short range order parameter, Eq. (72), to lend itself directly to a comparison with η. This was pointed out in Part (4) of this section when we derived an approximate relation between the correct analog, Eq. (76), and Eq. (78). For comparison with the short range order parameter, we have included a table of ρ^2, Table VII, which is based on the approximate relation, Eq. (79).

8. Comparison of the Theoretical Long Range Order with Experiment

There are two experimental determinations of the sublattice magnetization in real antiferromagnets in the literature. They correspond to the measurement of the sublattice magnetization in a body-centered cubic spin 5/2 system,[34] (the magnetic lattice in MnF_2), and of the sublattice magnetization in a simple cubic spin 5/2 system,[35] (the magnetic lattice in $KMnF_3$).

The body-centered lattice, while of the two sublattice structure, has not been discussed heretofore because

of its essentially different nearest neighbor structure. In the three lattices which have been considered, i.e., linear chain, plane quadratic, and simple cubic, the positions of the nearest neighbors define an orthogonal coordinate system, and hence the δ are linearly independent. This is not true of the δ corresponding to the body-centered lattice, and hence greater care must be taken in determining the values of the sums over the reciprocal lattice which lead from Eqs. (47) and (52) to the values of the C_2 and C_4 of Eq. (54). Thus, substitution of $\gamma_0 = 8$ in Eq. (54) does not lead to the values of C_2 and C_4 which are characteristic of the body-centered lattice. As a result, we omit discussion of this case here, except to say that there is an apparent discrepancy between the experimental result, (ρ=1.00±0.02), and the spin wave prediction, (ρ=0.976). This same type of discrepancy appears in the simple cubic case, ($KMnF_3$), and here direct comparison with the theory as presented in this dissertation can be made.

The experimentally measured sublattice magnetization in $KMnF_3$ has been determined to be $\rho = 0.998 \pm 0.015$. From Table VI, we obtain for the results of this dissertation, $\rho = 0.977$, and for the spin wave theory, $\rho = 0.969$. The results of the spin wave theory are clearly in disagreement with the experimental results, while the results of this work lie just outside the possible experimental

error. With the calculation of additional terms of the perturbation series, Eq. (82), it might be hoped ρ would converge to a limit lying within the interval indicated by experiment. That such is probably not the case is shown by the following argument.

We consider the contribution made to the terms D_2 and D_4, appearing in the perturbation series for the sublattice magnetization, i.e., Eq. (54), by the terms of the overlap, Eq. (90). Thus we have for D_2 and D_4 in this approximation, using the results of Eq. (90), and putting $S = 5/2$, $\gamma_0 = 6$,

$$D_2 \cong \frac{1}{S\gamma_0} d_{11} + \frac{1}{(S\gamma_0)^2} d_{12} \tag{91}$$

$$\cong 0.0178$$

and

$$D_4 \cong \frac{1}{S\gamma_0} d_{21} + \frac{1}{(S\gamma_0)^2} d_{22}$$

$$\cong 0.0050.$$

Comparison of these approximate values with the exact values of Table V show D_2 and D_4 to be given correctly by the overlap terms to within 2%. If we assume this relationship to hold for arbitrary D_n, then an upper limit to the <u>deviation</u> from perfect order lies within 2% of the

corrected spin wave deviation, and a lower limit to the deviation is given by the present theory to fourth order. Thus,

$$0.968 < \rho < 0.977. \tag{92}$$

Of course, Eq. (92) is by no means rigorous, but it seems to reflect the general trend of the perturbation series for the sublattice magnetization.

The disagreement of the sublattice magnetization predictions of both the corrected spin wave theory and the perturbation theory with those of experiment thus is not resolved. Considerations of canting in $KMnF_3$, as well as of anisotropy, fail to account for the difference. Canting has been shown to have a negligible effect on the spin wave spectrum for the degree of canting present in $KMnF_3$.[36] The anisotropy field, H_A, in $KMnF_3$ is of the order of 4 oe, while the exchange field, H_E, is of the order of 1.6×10^6 oe.[37] The relationship between the anisotropy parameter a, H_A, and H_E for the sublattice magnetization is given by

$$a = \frac{H_A}{H_E + H_A}. \tag{93}$$

Eq. (93) is based upon the way in which a, H_A, and H_E enter into the spin wave expression for the sublattice

magnetization. Thus a is of the order of 10^{-6} for $KMnF_3$, clearly too small to affect our determination of ρ.

Experiments involving the determination of the sublattice magnetization for spin one-half systems, e.g., $CuCl_2 \cdot 2H_2O$, where the theoretical deviation is much larger, may make more clear how to correlate theory and experiment.

E. Convergence Properties of the Ground State Parameter Series Approximations

To begin with, almost nothing can be said about the convergence of series for which the form of the general term is not known. Of the antiferromagnetic ground state parameter series, the form of the general term is known only for the energy and short range order series corresponding to the linear chain with spin one-half.[19] In this case, both series are very noisy, i.e., have no apparent pattern for the sign of succeeding terms, and the convergence properties are not readily assessable. For the perturbation series developed in this dissertation, the discussion of the convergence properties will have to be limited to comparison with the spin wave series, along with comments on the relative magnitudes of succeeding terms.

1. <u>The Spin Wave Series</u>

We list below the series approximations obtained from the corrected spin wave theory for the ground state parameters. The subscripts on the parameter symbols refer to the dimensionality of the lattice, i.e., linear chain, plane quadratic, and simple cubic.

$$\frac{E}{E_0}_{D=1} = 1 + 0.7268\left(\frac{1}{2S}\right) + 0.1321\left(\frac{1}{2S}\right)^2 + \ldots, \quad (94)$$

$$\frac{E}{E_0}_{D=2} = 1 + 0.316\left(\frac{1}{2S}\right) + 0.025\left(\frac{1}{2S}\right)^2 + \ldots,$$

$$\frac{E}{E_0}_{D=3} = 1 + 0.194\left(\frac{1}{2S}\right) + 0.009\left(\frac{1}{2S}\right)^2 + \ldots,$$

$$\eta_{D=2} = -1 + 0.786\left(\frac{1}{2S}\right) - 0.756\left(\frac{1}{2S}\right)^2 + \ldots, \quad (95)$$

$$\eta_{D=3} = -1 + 0.312\left(\frac{1}{2S}\right) - 0.168\left(\frac{1}{2S}\right)^2 + \ldots,$$

$$\rho_{D=2} = 1 - 0.394\left(\frac{1}{2S}\right) - 0.000\left(\frac{1}{2S}\right)^2 + \ldots, \quad (96)$$

$$\rho_{D=3} = 1 - 0.156\left(\frac{1}{2S}\right) - 0.000\left(\frac{1}{2S}\right)^2 + \ldots,$$

2. <u>The Perturbation Series</u>

For comparison with Eqs. (94), (95), and (96), we pick the spin one-half and spin two cases from Tables II and V.

$$\left.\frac{E}{E_0}\right|_{\substack{D=1\\S=1/2}} = 1 + (1-a)^2 - 0.2500\ (1-a)^4 + \ldots, \tag{97}$$

$$\left.\frac{E}{E_0}\right|_{\substack{D=1\\S=2}} = 1 + 0.1429(1-a)^2 + 0.0456(1-a)^4 + \ldots,$$

$$\left.\frac{E}{E_0}\right|_{\substack{D=2\\S=1/2}} = 1 + 0.0333(1-a)^2 - 0.0065(1-a)^4 + \ldots,$$

$$\left.\frac{E}{E_0}\right|_{\substack{D=2\\S=2}} = 1 + 0.0667(1-a)^2 + 0.0078(1-a)^4 + \ldots,$$

$$\left.\frac{E}{E_0}\right|_{\substack{D=3\\S=1/2}} = 1 + 0.2000(1-a)^2 - 0.0008(1-a)^4 + \ldots,$$

$$\left.\frac{E}{E_0}\right|_{\substack{D=3\\S=2}} = 1 + 0.0435(1-a)^2 + 0.0037(1-a)^4 + \ldots,$$

$$\eta_{\substack{D=2\\S=1/2}} = -1 + 0.3333(1-a)^2 - 0.0195(1-a)^4 + \ldots, \tag{98}$$

$$\eta_{\substack{D=2\\S=2}} = -1 + 0.0667(1-a)^2 + 0.0234(1-a)^4 + \ldots,$$

$$\eta_{\substack{D=3\\S=1/2}} = -1 + 0.2000(1-a)^2 - 0.0024(1-a)^4 + \ldots,$$

$$\eta_{\substack{D=3\\S=2}} = -1 + 0.0435(1-a)^2 + 0.0111(1-a)^4 + \ldots,$$

$$\rho_{\substack{D=2\\S=1/2}} = 1 - 0.2222(1-a)^2 - 0.0356(1-a)^4 - \ldots, \tag{99}$$

$$\rho_{\substack{D=2\\S=2}} = 1 - 0.0356(1-a)^2 - 0.0136(1-a)^4 - \ldots,$$

$$\rho_{\substack{D=3\\S=1/2}} = 1 - 0.1200(1-a)^2 - 0.0081(1-a)^4 - \ldots,$$

$$\rho_{\substack{D=3\\S=2}} = 1 - 0.0227(1-a)^2 - 0.0061(1-a)^4 - \ldots$$

The apparent convergence of the perturbation series is relatively faster than that of the corresponding spin wave series when the spin is small. This judgment is made solely on the basis of the magnitude of the ratio

formed from the last two terms of each series. The notable exception to this rule occurs in the case of the sublattice magnetization parameter, where the first order correction to the spin wave theory is in all cases zero. Higher order corrections are not necessarily zero, however, and if they were available, the relative convergence could be discussed for this parameter in terms of them.

IV. PERTURBATION THEORY OF THE HEISENBERG ANTIFERROMAGNET AT LOW TEMPERATURES

A. The Partition Function

We now turn to the consideration of the partition function for a Heisenberg antiferromagnet. Kubo[38] has given a perturbation expansion of the partition function which is particularly suited to the extension of the previous treatment of the ground state to include excited states as well. According to Kubo,

$$\exp(-\beta H) = \frac{1}{2\pi i}\oint \frac{\exp(-\beta E)}{E - H_0} \sum_{m=0}^{\infty} \left(H_1 \frac{1}{E - H_0}\right)^m dE, \tag{100}$$

where $H = H_0 + H_1$.

1. Zero Order and Perturbation Hamiltonians

Since H_0 is an operator, we need a definition for the operator $1/(E-H_0)$. We shall be concerned with the trace of Eq. (100) with respect to a complete set of eigenfunctions of H_0, for which the definition of $1/(E-H_0)$ is immediate. If we identify the zero order and perturbation Hamiltonians with the division of the Hamiltonian used in the ground state perturbation calculation of Chapter III, then we have the division indicated in Eq. (21).

We may think of H_0 and H_1 as expressed in lattice space or in reciprocal lattice space, i.e., in the form of Eq. (2), Chapter II, or of Eq. (22), Chapter III, respectively. For convenience in defining a complete set of eigenfunctions for H_0, we use the Hamiltonian in the form of Eq. (2). For calculational purposes, however, we will insert the transformation to reciprocal lattice space. Thus the eigenfunctions of H_0 all take the form

$$\phi(n, n_1 n_2) = |n, n_1 n_2\rangle \tag{101}$$

where $|n, n_1 n_2\rangle$ represents a normalized eigenstate of H_0 in which there are n deviations from the Neel state, n_1 of them on sublattice #1, and n_2 of them on sublattice #2. Thus $n_1 + n_2 = n$. We do not here explicitly differentiate among the many different configurations of the n_1 and n_2 deviations, although this difference will figure importantly in later calculations.

2. <u>The Partition Function to Second Order</u>

The trace of Eq. (100) with respect to the states of Eq. (101) is indicated by

$$\mathrm{Tr}[\exp(-\beta H)] = \sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n, n_1 n_2 | \frac{1}{2\pi i} \oint \exp(-\beta E) \tag{102}$$

$$\times \sum_{m=0}^{\infty} \left[\frac{1}{E - H_0} H_1\right]^m \frac{1}{E - H_0} dE \, |n, n_1 n_2\rangle.$$

We now propose to expand Eq. (102) explicitly in terms of the operators D and U. Since U raises the number of excitations, n, and D lowers n, and because the states of Eq. (101) are orthogonal in n, it follows that all non-vanishing elements of the trace must have the number of D operators equal to the number of U operators. Thus for zeroth order, we have no D or U operators. The first order correction vanishes, and the second order contains one D and one U operator. The third order vanishes, and the fourth order contains two D and two U operators, etc. Thus

$$\mathrm{Tr}[\exp(-\beta H)] = \sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n, n_1 n_2 | \frac{1}{2\pi i} \oint \exp(-\beta E) \tag{103}$$

$$\times \left\{ \sum_{m=0}^{\infty} \left(\frac{1}{E-H_0} I\right)^m \frac{1}{E - H_0} \right.$$

$$+ \sum_{m=0}^{\infty} \left(\frac{1}{E-H_0} I\right)^m \frac{1}{E - H_0} D \sum_{p=0}^{\infty} \left(\frac{1}{E-H_0} I\right)^p \frac{1}{E - H_0} U$$

$$\times \sum_{q=0}^{\infty} \left(\frac{1}{E-H_0} I\right)^q \frac{1}{E - H_0} + \sum_{m=0}^{\infty} \left(\frac{1}{E-H_0} I\right)^m \frac{1}{E - H_0} U$$

$$\left. \times \sum_{p=0}^{\infty} \left(\frac{1}{E-H_0} I\right)^p \frac{1}{E - H_0} D \sum_{q=0}^{\infty} \left(\frac{1}{E-H_0} I\right)^q \frac{1}{E - H_0} + \ldots \right\} | n, n_1 n_2 \rangle .$$

in which the zeroth and second orders have been indicated explicitly.

The solution to Eq. (103) in zeroth order is identical with that of the Ising model, $H = H_0 + I$. The fact that we do not know how to write down this solution in three dimensions will not present a great deal of difficulty in the low temperature expansion to be derived from Eq. (103).

In order to develop a low temperature expansion of Eq. (103), we investigate it as a function of $\exp(-\beta\Delta/2)$, since with $\beta = 1/kT$, $\Delta > 0$,

$$\lim_{T\to 0} \exp(-\beta\Delta/2) \to 0. \tag{104}$$

Since the states of Eq. (101) are also eigenstates of $H_0 + 1$, we may re-express the zeroth order of Eq. (103),

$$\mathrm{Tr}[\exp(-\beta H)]_{\text{zeroth order}} \tag{105}$$

$$= \sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n, n_1 n_2 | \frac{1}{2\pi i} \oint \frac{\exp(-\beta E)}{E - E_M - I} \times dE | n, n_1 n_2 \rangle,$$

where $E_n = E_0 + n\Delta/2$. Evaluation of the integral yields

$$\mathrm{Tr}[\exp(-\beta H)]_{\text{zeroth order}} = \exp(-\beta E_0)\Big\{1 \tag{106}$$

$$+ \exp(-\beta\Delta/2) \sum_{n_1+n_2=1} \langle 1, n_1 n_2 | \exp(-\beta I) | 1, n_1 n_2 \rangle$$

$$+ \exp(-\beta\Delta) \sum_{n_1+n_2=2} \langle 2, n_1 n_2 | \exp(-\beta I) | 2, n, n_2 \rangle + \ldots \Big\},$$

where the expansion in powers of $\exp(-\beta\Delta/2)$ has been made explicit.

In the second order of Eq. (103), we may also re-express the terms in a form similar to Eq. (105), but now, for convenience of expression, it is desirable to place subscripts on the operator I which denote the sequence in which all operators, D, I, and U, are applied. That is, I_0 means that I is applied to the original eigenfunction, $|n, n_1 n_2\rangle$. I_1 is applied after the operator U is attached to $|n, n_1 n_2\rangle$. I_{-1} is applied after the operator D is attached to $|n, n_1 n_2\rangle$, etc. Thus we have for the second order correction,

$$\sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n, n_1 n_2 | \frac{1}{2\pi i} \oint \exp(-\beta E) dE \tag{107}$$

$$\times \frac{1}{E - E_n - I_0} D \frac{1}{E - E_{n+2} - I} U \frac{1}{E - E_n - I_0} | n, n_1 n_2 \rangle$$

$$= \exp(-\beta E_0) \Big\{ \langle 0 | [- D \frac{1}{(\Delta + I_1 - I_0)^2} U \exp(-\beta I_0)$$

$$+ \beta D \frac{1}{(\Delta + I_1 - I_0)} U \exp(-\beta I_0)] | 0 \rangle$$

$$+ \exp(-\beta\Delta/2) \sum_{n_1+n_2=1} \langle 1,n_1n_2| [- D\frac{1}{(\Delta+I_1-I_0)^2} U \exp(-\beta I_0)$$

$$+ \beta D\frac{1}{(\Delta+I_1-I_0)} U \exp(-\beta I_0)] |1,n_1n_2\rangle + \ldots ,$$

and

$$\sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n,n_1n_2| \frac{1}{2\pi i} \oint \exp(-\beta E) dE \tag{108}$$

$$\times \frac{1}{E - E_n - I_0} U \frac{1}{E - E_{n-2} - I_{-1}} D \frac{1}{E - E_n - I_0} |n,n_1n_2\rangle$$

$$= \exp(-\beta E_0) \Big\{ \sum_{n_1+n_2=2} \langle 2,n,n_2| U \exp(-\beta I_{-1}) D \frac{1}{(\Delta+I_0-I_1)^2}$$

$$|2,n,n_2\rangle$$

$$+ \exp(-\beta\Delta/2) \sum_{n_1+n_2=3} \langle 3,n_1n_2| U \exp(-\beta I_{-1}) D \frac{1}{(\Delta+I_0-I_{-1})^2}$$

$$|3,n_1n_2\rangle + \ldots ,$$

where we have carried out the expansion to the first power in $\exp(-\beta\Delta/2)$.

Thus, collection all terms of Eqs. (106), (107), and (108), and using the relationships

$$I|0\rangle = 0; \; I|1,n_1n_2\rangle = 0, \tag{109}$$

which result from the fact I measures the interaction

between individual spin deviations from the Neel state, and consequently requires at least two deviations to give a finite measure. Eq. (109) will allow us to drop the subscripts on I in the expression for the partition function below, since there remains only one position in which I gives a non-zero result. Thus we have for the partition function in the low temperature limit, and to second order in D and U,

$$\mathrm{Tr}[\exp(-\beta H)]_{\text{to second order}} \tag{110}$$

$$= \exp(-\beta E_0)\Big\{1 = \langle 0|[-D\frac{1}{(\Delta+I)^2}U + \beta D\frac{1}{(\Delta+I)}U]|0\rangle$$

$$+ \sum_{n_1+n_2=2}\langle 2,n,n_2|UD\frac{1}{(\Delta+I)^2}|2,n,n_2\rangle + \ldots\Big\}$$

$$+ \exp[-\beta(E_0+\tfrac{\Delta}{2})]\Big\{N + \sum_{n_1+n_2=n}\langle 1,n,n_2|[-D\frac{1}{(\Delta+I)^2}U$$

$$+ \beta D\frac{1}{(\Delta+I)}U]|1,n_1n_2\rangle + \sum_{n_1+n_2=3}\langle 3,n_1n_2|UD\frac{1}{(\Delta+I)^2}3,n_1n_2\rangle$$

$$+ \ldots\Big\}$$

$$+ \exp[-\beta(E_0+\Delta)]\Big\{\sum_{n_1+n_2=2}\langle 2,n_1n_2|\exp(-\beta I)|2,n_1n_2\rangle + \ldots\Big\}$$

$$+ \ldots$$

Eq. (110) may be simplified by noticing that:

$$\langle 0|D\frac{1}{(\Delta+I)^n}U|0\rangle = \sum_{n_1+n_2=2}\langle 2,n_1n_2|UD\frac{1}{(\Delta+I)^n}|2,n_1n_2\rangle, \quad (111)$$

and

$$\sum_{n_1+n_2=1}\langle 1,n_1n_2|D\frac{1}{(\Delta+I)^n}U|1,n_1n_2\rangle =$$

$$\sum_{n_1+n_2=3}\langle 3,n_1n_2|UD\frac{1}{(\Delta+I)^n}|3,n_1n_2\rangle.$$

Using Eq. (111), we get for Eq. (110),

$$\begin{aligned}
&\mathrm{Tr}[\exp(-\beta H)]_{\text{to second order}} \qquad (112)\\
&= \exp(-\beta E_0)\left\{1 + \beta\langle 0|D\frac{1}{\Delta+I}U|0\rangle + \ldots\right\}\\
&+ \exp[-\beta(E_0+\tfrac{\Delta}{2})]\left\{N + \beta\sum_{n_1+n_2=1}\langle 1,n_1n_2|D\frac{1}{(\Delta+I)}U\right.\\
&\qquad \left.|1,n_1n_2\rangle + \ldots\right\}\\
&+ \exp[-\beta(E_0+\Delta)\left\{\sum_{n_1+n_2=2}\langle 2,n_1n_2|\exp(-\beta I)|2,n_1n_2\rangle\right.\\
&\qquad \left. + \ldots\right\}\\
&+ \ldots
\end{aligned}$$

3. Relationship Between the Partition Function Expansion and the Ground State Energy Series

Examining the first term in Eq. (112), we note that it appears to be a power series expansion of an exponential in which the argument is just the ground state

energy perturbation series derived in Chapter III, Eq. (32).

$$\langle 0| \exp[-\beta(E_0 - D\frac{1}{(\Delta+I)}U + \ldots)]|0\rangle \tag{113}$$

$$= \langle 0| \exp(-\beta E_0)[1 + \beta D\frac{1}{(\Delta+I)}U + \ldots]|0\rangle.$$

In Appendix C, we examine the fourth order perturbation terms of Eq. (102), and find that Eq. (113) is valid to this order also.

Thus, assuming the complete validity of Eq. (113) to all orders, the term which in zeroth order corresponds to $(-\beta E_0)$, goes over the $\exp(-\beta E_{\text{ground state}})$, which is to be expected.

B. <u>The Excited States</u>

1. <u>Perturbation Treatment for the General Case</u>

Examining the terms in Eq. (112) which in zeroth order correspond to $\exp[(-\beta(E_0 + \frac{\Delta}{2}))]$, we find

$$\sum_{n_1+n_2=1} \langle 1,n_1n_2| \left\{\exp[-\beta[E_0 + \frac{\Delta}{2} - D\frac{1}{(\Delta+I)}U + \ldots]\right\}|1,n_1n_2\rangle \tag{114}$$

$$= \sum_{n_1+n_2=1} \langle 1,n_1n_2|\exp[-\beta(E_0 + \frac{\Delta}{2})]\ 1 + \beta D\frac{1}{(\Delta+I)}U$$

$$+ \ldots\Big\}|1,n_1n_2\rangle,$$

under assumptions similar to those leading to Eq. (113).

In Appendix C, Eq. (114) is also shown to be valid through fourth order.

Eq. (114) does not make plain the relationship of the excited states to the ground state, but an explicit calculation will serve to do so. We take for the normalized eigenstates $|1,n_1n_2\rangle$,

$$|1,1,0\rangle = \frac{1}{\sqrt{2S}}S_j^-|0\rangle = \frac{1}{\sqrt{2S}}\left(\frac{2}{N}\right)^{1/2}\sum_{\lambda}\exp(-i\lambda\cdot j)S_{\lambda_1}^-|0\rangle, \qquad (115)$$

$$|1,0,1\rangle = \frac{1}{\sqrt{2S}}S_k^+|0\rangle\ 2\ \frac{1}{\sqrt{2S}}\left(\frac{2}{N}\right)^{1/2}\sum_{\lambda}\exp(-i\lambda\cdot k)S_{-\lambda_2}^+|0\rangle.$$

Substitution of Eq. (115) into Eq. (114) yields

$$\sum_{n_1+n_2=1}\langle 1,n_1n_2|\exp[-\beta(E_0+\tfrac{\Delta}{2})]\left\{1+\beta D\frac{1}{\Delta+I}U+\ldots\right\}|1,n_1n_2\rangle \qquad (116)$$

$$= \exp[-\beta(E_0+\tfrac{\Delta}{2})]\left\{N+\frac{\beta}{2S}\sum_{\lambda}\sum_{m=0}^{\infty}[\langle 0|S_{-\lambda_1}^+D\frac{(-I)^m}{\Delta^{m+1}}US_{\lambda_1}^-|0\rangle\right.$$

$$\left.+\langle 0|S_{\lambda_2}^-D\frac{(-I)^m}{\Delta^{m+1}}US_{-\lambda_2}^+|0\rangle+\ldots]\right\},$$

where we have made use of the Kronecker delta relationships,

$$\sum_j \exp(i(\lambda-\lambda')\cdot j] = \delta_{\lambda,\lambda'}, \qquad (117)$$

$$\sum_k \exp[i(\lambda-\lambda')\cdot k] = \delta_{\lambda,\lambda'}.$$

The validity of the binomial expansion of the term involving the operator I depends, of course, upon the condition that the expectation value of I/Δ have a magnitude of less than unity. For the states involved in Eq. (114), this condition will be fulfilled except for the linear chain with spin one-half, which we treat separately later.

The symmetry of the operators D, I, and U with respect to the sublattices indicate that both terms of the sum over the reciprocal lattice in Eq. (116) are equal. Therefore, we calculate only one of these. For the effect of the operator I on $US_{\lambda_1}^{-}|0>$, we have by means of the definition of I given in Eq. (20),

$$(-I)^m S_{\lambda_1}^{-}|0< = (2J)^m US_{1}^{-}|0> \tag{118}$$

$$+ (2J)^m(2^m-1)J(1-a)(\tfrac{2}{N})\sum_{\mu\beta}\gamma_\mu\gamma_\beta$$

$$\times (S_{\beta_1}^{-})(S_{-\beta_2-\mu_2}^{+})(S_{\lambda_1+\mu_1}^{-})|0>.$$

Insertion of Eq. (118) into Eq. (116), with the subsequent commutation of $S_{-\lambda_1}^{+}$ operator through all operators until it operates on $S_{\lambda_1}^{-}$, and the final evaluation of the resulting terms, yields

$$\sum_{n_1+n_2=1} <1,n_1n_2|\exp[-\beta(E_0 + \tfrac{\Delta}{2})]\left\{1 + \beta D\frac{1}{\Delta + I}U + \ldots\right\}|1,n_1n_2> \tag{119}$$

$$= \exp[-\beta(E_0 + \tfrac{\Delta}{2})]\Big\{N + N\beta[\frac{\langle DU\rangle}{\Delta - 2J} + \frac{4J^2(1-a)^2}{\Delta - 2J}(S\gamma_0)$$

$$\times\ (1-(s\gamma_0)(\tfrac{2}{N})\sum_\lambda \frac{\gamma_\lambda^2}{\gamma_0^2}) + \frac{8J^3(1-a)^2}{(\Delta-2J)(\Delta-4J)}(S\gamma_0)(1-(S\gamma_0)$$

$$-(S\gamma_0)(\tfrac{2}{N})\sum_\lambda \frac{\gamma_\lambda^2}{\gamma_0^2})] = \ldots\Big\}.$$

Reversing the process indicated in Eq. (114) allows us to write for the energy of the first excited states,

$$E_{\text{first excited states}} = N\Big\{E_0 - \frac{\langle DU\rangle}{\Delta - 2J} + \ldots \qquad (120)$$

$$+ \tfrac{\Delta}{2}[1 + \frac{(1-a)^2}{2(2S\gamma_0-1)} - \frac{(1-a)^2(S\gamma_0)}{2(S\gamma_0-1)}(\tfrac{2}{N})\sum_\lambda \frac{\gamma_\lambda^2}{\gamma_0^2} + \ldots]\Big\}.$$

Eq. (120) indicates that there are N first excited states, each of which lies near the ground state, as indicated by the presence of the ground state energy perturbation series appearing in Eq. (120). The incremental difference between the ground state and the first excited states is given by the terms proportional to $\Delta/2$ in Eq. (120). There are N/2 different increments, each characterized by a different λ. Thus each λ corresponds to a doubly degenerate energy level. The dispersion relation for the first excited states in this second order approximation is then given by the relationship between the incremental energy and the reciprocal lattice wave vectors λ.

$$\Delta E_{\text{first excited states}} \tag{121}$$

$$= \frac{\Delta}{2}\left[1 + \frac{(1-a)^2}{2(2S\gamma_0-1)} - \frac{(1-a)^2(S\gamma_0)}{2(S\gamma_0-1)}\frac{\gamma_\lambda^2}{\gamma_0^2} + \ldots\right].$$

2. Comparison with Spin Wave Theory

The first excited state energy derived by means of the spin wave theory is given by[11]

$$\Delta E_{\text{first excited states}} = \frac{\Delta}{2}\left[1 - \frac{\gamma_\lambda^2}{\gamma_0^2}(1-a)^2\right]^{1/2}. \tag{122}$$

Examination of Eq. (121) for large spin, (the condition of validity for the spin wave theory), reveals Eq. (121) to be the first two terms of a binomial expansion of Eq. (122). This is precisely the kind of relation which we found for the comparison of the perturbation and spin wave treatments of the ground state. There is an important difference, however, which affects the usefulness of Eq. (121).

The relative merits of the spin wave approximation versus the perturbation technique for the determination of the low temperature properties of real antiferromagnets depend upon the amount of anisotropy present. The very nature of the perturbation technique indicates its applicability to antiferromagnets with strong anisotropy. The zero order Hamiltonian represents the complete suppression

of any contribution from the off-axis components of the spin, and in order to represent the isotropic Hamiltonian, the contribution from the off-axis components must be completely restored. In the ground state problem, it was unnecessary to go this far in order to achieve an excellent representation for the energy, and relatively good representations of the short and long range order. In the case of the excited states, however, because of the Boltzmann factor, greater importance is attached to the lowest energy eigenstates of Eq. (121), and it is just these states which are most affected by the presence of an anisotropy. A finite anisotropy, no matter how small, removes the degeneracy between the lowest of the excited state energies and the energy of the ground state, thereby introducing an energy gap.[39]

The ground state is adequately represented by a few orders of the perturbation because its deviation from the Neel state is determined by a sum of unweighted contributions from all of the modes of the lattice. The term "unweighted" is used here to indicate the absence of a Boltzmann factor in the ground state sum. The relatively poor representation of the adjustment in the ground state energy via zero-point fluctuations associated with a long wavelength, which give only a small contribution to the total adjustment of the ground state energy because of the nearly perfect alignment of spins in a long wavelength

mode, are easily compensated for by the much more adequate representation of the short wavelength, high energy zero point fluctuations. This property of the perturbation expansion is of little avail when it comes to determining the low temperature behavior of an antiferromagnet, where it is the low energy, long wavelength modes which are most important.

The important properties of both the perturbation and spin wave treatments of the excited states can best be seen when compared with the one exact treatment for these states.[40] This may be done as soon as our treatment of the general case is extended to the case of the linear chain with spin one-half.

3. Perturbation Treatment for the Linear Chain with Spin One-Half

We now return to the development of our perturbation series at the point of Eqs. (107) and (108). Here we must regard the fact that for some states of the linear chain coupled with spin one-half, all three energy denominators are equal. This is reflected in the fact that the binomial expansion used in Eq. (116) is not valid for these states, and consequently the expression in Eq. (119) cannot be evaluated for $S = 1/2$, $\gamma_0 = 2$. Instead of tacitly assuming that the middle energy denominator of Eqs. (107) and (108) differs from the other two, we evaluate the integrals in the following manner.

$$\sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n, n_1 n_2 | \frac{1}{2\pi i} \oint \exp(-\beta E)\, dE \tag{123}$$

$$\times \frac{1}{E - H_0 - I} D \frac{1}{E - H_0 - I} U \frac{1}{E - H_0 - I} | n, n_1 n_2 \rangle$$

$$= \sum_{n=0}^{N} \sum_{n_1+n_2=n} \frac{\partial}{\partial(E_0 + \frac{n\Delta}{2} + I_0)} \frac{1}{2\pi i} \oint \exp\ (-\beta E)\, dE$$

$$\times D \frac{1}{E - [E_0 + \frac{(n+2)\Delta}{2} + I_1]} U \frac{1}{E - (E_0 + \frac{n\Delta}{2} + I_0)} | n, n_1 n_2 \rangle$$

$$= \sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n, n_1 n_2 | DU \left\{ \frac{\exp[-\beta(E_0 + \frac{(n+2)\Delta}{2} + I_1)]}{[E_0 + \frac{(n+2)\Delta}{2} + I_1 - (E_0 + \frac{n\Delta}{2} + I_0)]^2} \right.$$

$$\frac{-\exp[-\beta(E_0 + \frac{n\Delta}{2} + I_0)]}{[E_0 + \frac{(n+2)\Delta}{2} + I_1 - (E_0 + \frac{n\Delta}{2} + I_0)]^2}$$

$$\left. \frac{-\beta \exp[-\beta(E_0 + \frac{n\Delta}{2} + I_0)]}{[E_0 + \frac{n\Delta}{2} + I_0 - (E_0 + \frac{(n+2)\Delta}{2} + I_1)]} \right\} | n, n_1 n_2 \rangle$$

which, in the limit as $I_1 + \Delta \rightarrow I_0$, i.e., when all three energy denominators are equal,

$$= \lim_{I_0 \rightarrow I_1 + \Delta} \sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n, n_1 n_2 | DU$$

$$x\left\{\frac{-\beta\exp[-\beta(E_0+\frac{n\Delta}{2}+I_0)]}{E_0+\frac{n\Delta}{2}+I_0-(E_0+\frac{(n+2)\Delta}{2}+I_1)}\right\}|n,n_1n_2>.$$

In place of Eq. (108), we get

$$\lim_{I_0+\Delta\to I_{-1}}\sum_{n=0}^{N}\sum_{n_1+n_2=n}<n,n_1n_2|UD \tag{124}$$

$$x\left\{\frac{-\beta\exp[-\beta(E_0+\frac{n\Delta}{2}+I_0)]}{E_0+\frac{n\Delta}{2}+I_0-(E_0+\frac{(n-2)\Delta}{2}+I_1)}\right\}|n,n_1n_2>.$$

The term with $n = 1$ in Eq. (123), and the term with $n = 3$ in Eq. (124) provide us with the entire contribution which is proportional to $\exp[-\beta(E_0+\Delta/2)]$. In the limits indicated in Eqs. (123) and (124), this contribution vanishes. The vanishing of this term corresponds to the omission of the term in Eq. (119) which is proportional to $(\Delta-4J)^{-1}$. Thus we arrive at the following instead of Eq. (121)

$$\Delta E = 2J[1 + (1-a)^2 - (1-a)^2\frac{\gamma\lambda^2}{4}]. \tag{125}$$

In Figure 2, we show the dispersion curves for the spin one-half coupled linear chain in this approximation, the spin wave approximation, and the exact solution. From Figure 2, it is apparent that Eq. (125) best approximates

the exact solution in the short wavelength region, i.e., $\lambda|\delta| = \pi/2$. This bears out what was previously said with regard to the treatment of the ground state. For the treatment of the excited states, however, the large gap which is evident in Figure 2 between the lowest states and the ground state in this order of the perturbation, precludes the use of this theory to obtain meaningful low temperature thermodynamic behavior for real antiferromagnets. Higher order corrections are not likely to close this gap rapidly, in the sense that the presence of even a small gap profoundly modifies the low temperature behavior.

V. SUMMARY

Perturbation series for the ground state parameters of the Heisenberg antiferromagnet, i.e., the energy, short range order, and long range order, have been presented in a quite general form through fourth order in the perturbation Hamiltonian. The final zero order Hamiltonian is the Ising model, $H = 2J \sum_{<jk>} S_j^z S_k^z$, and the final perturbation Hamiltonian consists of the off-axis components of the interaction. The problem of the N-body divergence, present in any straightforward Rayleigh-Schrodinger perturbation treatment based on the Ising model, has been handled in a unique way. The choice of an initial zero order Hamiltonian other than the Ising model makes possible the generation of ordinary Rayleigh-Schrodinger perturbation series in which the N-body divergence is cancelled in each order, thus satisfying the requirement that a systematic method be used to eliminate non-physical contributions from the series. After the N-body divergence problem has been handled using the initial zero order Hamiltonian, a way is found to predict certain infinite classes of terms belonging to the original perturbation series. The inclusion of these terms in the perturbation correction is shown to be equivalent to a shifting of the definition of

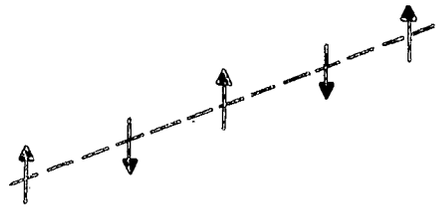
the zero order Hamiltonian to the Ising model.

The perturbation corrections to the energy, short range order, and long range order of the Neel state are exhibited as explicit functions of the spin and number of nearest neighbors, and also of an anisotropy parameter which essentially gives the order of the perturbation series. For comparison, equivalent expressions are derived for the standard spin wave treatment of the ground state. This procedure allows a complete analysis of the relationship between the two methods. On the basis of this analysis, it is found that the present method is superior to the spin wave method for the treatment of the ground state short range and long range order parameters in all one dimensional problems, and that it holds an advantage also in the treatment of the spin one-half cases in two and three dimensions.

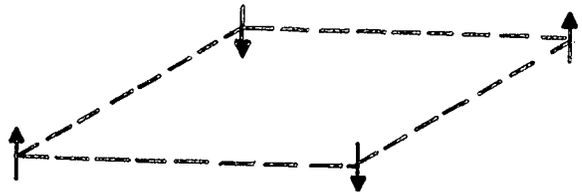
Experimental determinations of the sublattice magnetization in real antiferromagnets show a slightly larger value for the sublattice magnetization of the ground state than that predicted by either the perturbation technique presented in this dissertation, or the spin wave theory. Though the results of the perturbation treatment are closer to the experimental findings than are the results of the spin wave theory, complete confidence cannot be placed in the assumption that higher orders of the perturbation will not further lower the perturbation results. On the

basis of the analysis of the relationship between the two methods, it is reasonable to believe that the exact sublattice magnetization for the Heisenberg model ground state lies somewhere between the spin wave prediction and the perturbation prediction.

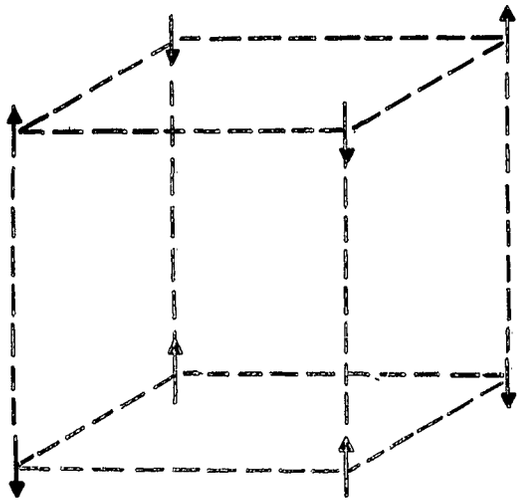
The treatment of the first excited states of the Heisenberg antiferromagnet by means of the perturbation theory show the anisotropy to have a strong influence upon the energies of the lowest of these states. Thus, beginning with a zero order Hamiltonian which is very anisotropic, and calculating only a few orders of the perturbation series, an adequate representation for the energies of these states is not found. It is concluded that one should rely on a continuation of the spin wave treatment of the states in the manner presented by Oguchi[32] for any improvement in the representation of the low lying excited states.



Linear Chain



Plane Quadratic



Simple Cubic

FIGURE 1. Classical Antiferromagnetic Ground States

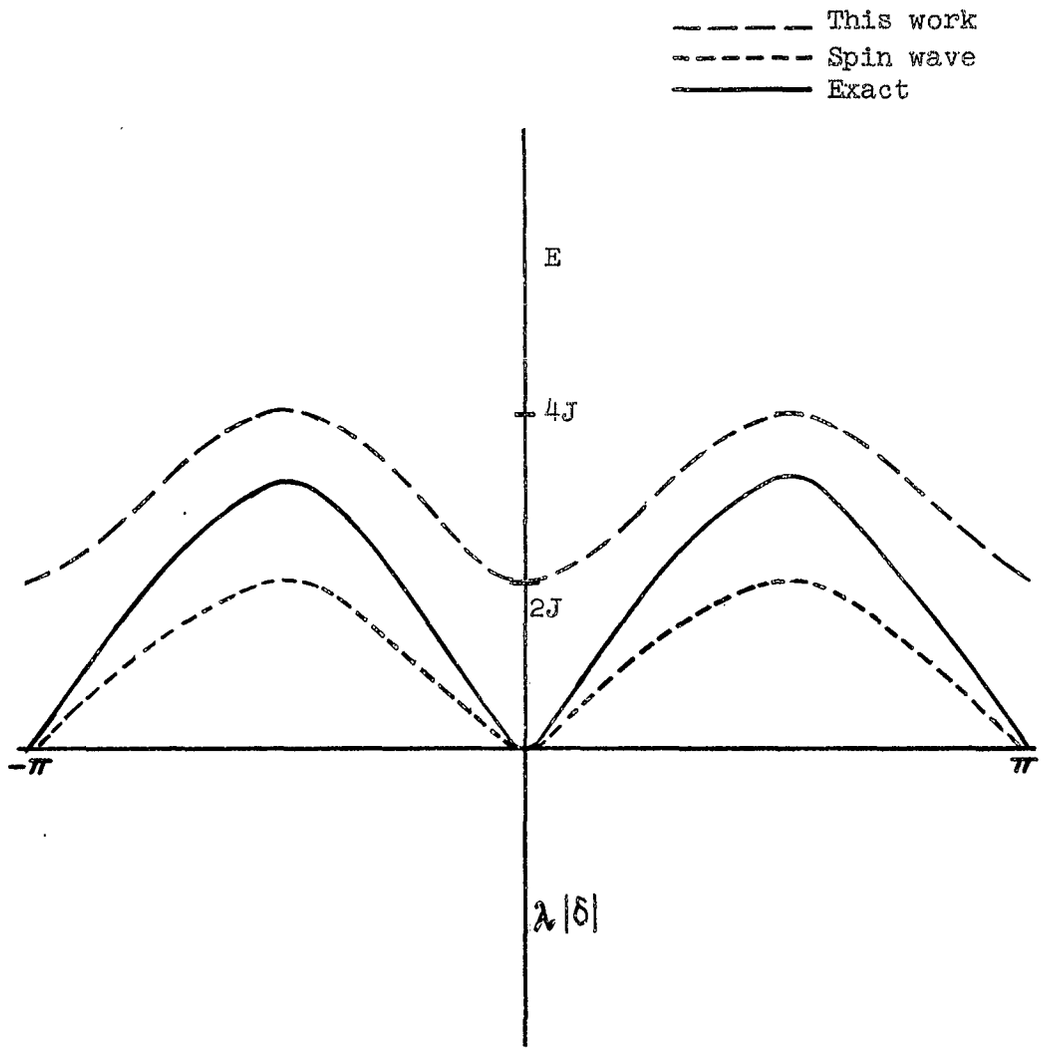


FIGURE 2. Dispersion Relation for the Linear Chain with Spin One-half

TABLE I

Qualitative Results of Previous Methods Used to Compute the Sublattice Magnetization of the Ground State

Is there a Finite Sublattice Magnetization?	Linear Chain		Plane Quadratic		Simple Cubic	
	S=1/2	S>1/2	S=1/2	S>1/2	S=1/2	S>1/2
Anderson	No	No	Yes	Yes	Yes	Yes
Kubo	Yes	Yes	Yes	Yes	Yes	Yes
Kasteleijn	No					
Taketa and Nakamura			No		No	
Marshall	No		No		No	
Fisher					Yes	Yes
Davis	Yes	Yes	Yes	Yes	Yes	Yes

TABLE II

The Perturbation Correction to the Energy

Lattice		C_2			
		S=1/2	S=1	S=3/2	S=2
Linear Chain:	This Work	1.0000	0.3333	0.2000	0.1429
	Linked Cluster	1.0000	0.3333	0.2000	0.1429
Plane Quadratic:	This Work	0.3333	0.1429	0.0909	0.0667
	Linked Cluster	0.3333	0.1429	0.0909	0.0667
Simple Cubic:	This Work	0.2000	0.0909	0.0588	0.0435
	Linked Cluster	0.2000	0.0909	0.0588	0.0435
		C_4			
Linear Chain:	This Work	-0.2500	0.0782	0.0591	0.0456
	Linked Cluster	-0.4590	0.0292	0.0284	0.0226
Plane Quadratic:	This Work	-0.0065	0.0251	0.0099	0.0078
	Linked Cluster	-0.0098	0.0123	0.0098	0.0078
Simple Cubic:	This Work	-0.0008	0.0055	0.0045	0.0037
	Linked Cluster	-0.0015	0.0054	0.0045	0.0037
		$E/E_0(a=0)$*			
Linear Chain:	This Work	1.7500	1.4115	1.2591	1.1885
	Linked Cluster I	1.5410	1.3625	1.2284	1.1655
	Linked Cluster II	1.7363	1.3567	1.2287	1.1686
Plane Quadratic:	This Work	1.3268	1.1680	1.1008	1.0745
	Linked Cluster I	1.3235	1.1552	1.1007	1.0745
	Linked Cluster II	1.3281	1.1563	1.1027	1.0765
Simple Cubic:	This Work	1.1992	1.0964	1.0633	1.0472
	Linked Cluster I	1.1985	1.0964	1.0633	1.0472
	Linked Cluster II	1.1996	1.0973	1.0643	1.0481

*The greater the magnitude of this term, the lower the corresponding energy, since $E, E_0 < 0$.

TABLE III

Comparison of the Perturbation and Spin Wave Corrections to the Energy

Lattice		$E/E_0(a=0)$			
		S=1/2	S=1	S=3/2	S=2
Linear Chain:	This Work	1.7500	1.4115	1.2591	1.1885
	Corrected Spin Wave*	1.8589	1.3964	1.2569	1.1900
	Hybrid Method	1.7651	1.4485	1.2903	1.2144
Plane Quadratic:	This Work	1.327	1.168	1.101	1.075
	Corrected Spin Wave	1.341	1.164	1.108	1.081
	Hybrid Method	1.322	1.177	1.109	1.081
Simple Cubic:	This Work	1.199	1.096	1.063	1.047
	Corrected Spin Wave	1.203	1.099	1.066	1.050
	Hybrid Method	1.199	1.099	1.066	1.049

*Spin wave approximation + first order correction.

TABLE IV

Comparison of the Perturbation and
Spin Wave Corrections to the Short Range Order

Lattice	$-\eta(a=0)$			
	S=1/2	S=1	S=3/2	S=2
Linear Chain: This Work	0.7500	0.4321	0.6227	0.7203
Plane Quadratic: This Work	0.686	0.782	0.879	0.910
Corrected Spin Wave	0.970	0.796	0.822	0.850
Hybrid Method	1.038	0.763	0.822	0.851
Simple Cubic: This Work	0.802	0.907	0.928	0.945
Corrected Spin Wave	0.856	0.886	0.915	0.933
Hybrid Method	0.877	0.903	0.916	0.933

TABLE V

The Second and Fourth Order Corrections to the Long Range Order

Lattice	S=1/2	S=1	S=3/2	S=2	S=5/2
			D_2		
Linear Chain	1.0000	0.2222	0.1200	0.0816	
Plane Quadratic	0.2222	0.0816	0.0496	0.0356	
Simple Cubic	0.1200	0.0496	0.0311	0.0227	0.0178
			D_4		
Linear Chain	0.2500	0.1433	0.0687	0.0458	
Plane Quadratic	0.0356	0.0270	0.0181	0.0136	
Simple Cubic	0.0080	0.0107	0.0083	0.0061	0.0050
			$\rho(a=0)$		
Linear Chain	-0.2500	0.6345	0.8113	0.8726	
Plane Quadratic	0.7422	0.8914	0.9323	0.9509	
Simple Cubic	0.8720	0.9397	0.9606	0.9712	0.9772

TABLE VI

Perturbation and Spin Wave Corrections to the Long Range Order of the Isotropic Ground State

Lattice	$\rho(a=0)$ S=1/2	S=1	S=3/2	S=2	S=5/2
Linear Chain:					
This Work	-0.2500	0.6345	0.8113	0.8726	
Plane Quadratic:					
This Work	0.7422	0.8914	0.9323	0.9509	
Corrected Spin Wave	0.607	0.803	0.869	0.902	
Hybrid Method	0.597	0.801	0.868	0.902	
Overlap	0.752	0.893	0.933	0.951	
Simple Cubic:					
This Work	0.8720	0.9397	0.9606	0.9712	0.9772
Corrected Spin Wave	0.844	0.922	0.948	0.961	0.969
Hybrid Method	0.848	0.922	0.948	0.960	0.969
Overlap	0.868	0.940	0.961	0.972	0.977

TABLE VII

The Square of the Long Range Order Parameter for Comparison with the Short Range Order Parameter

Lattice	$\rho^2(a=0)$			
	S=1/2	S=1	S=3/2	S=2
Linear Chain: This Work	--	0.403	0.658	0.761
Plane Quadratic: This Work	0.551	0.794	0.869	0.904
Simple Cubic: This Work	0.760	0.884	0.924	0.943

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APPENDIXES

APPENDIX A

In this Appendix we calculate the sixth order energy correction. For the general case with arbitrary spin and lattice, we proceed as far as the sixth order equivalent of Eq. (52), Chapter III. For the case of the linear chain with spin one-half, we continue on to determine explicitly the sixth order energy correction, which is found to be identical to that found for this case by a different method.[19] The desirability of such an effort lies with its implication that we have indeed recovered the Ising model as a zero order Hamiltonian, at least through six orders of the perturbation.

We begin by considering Eq. (53), Chapter III. By applying the relationships indicated in Eq. (40) and (51), the operators I which are superscripted with the symbols p, r, s, and q may be replaced by the explicit expression of their effects upon the U and D operators of the matrix elements. In performing this replacement, we are aided by the Hermitian property of the matrix elements, in particular by the fact that $\langle 0|DI^pDI^r| = (|I^rUI^pU|0\rangle)^+$. Following this replacement, the sums over p, r, s, and q may be performed to give in place of Eq. (53),

$$E^{(1-a)^6} = -\frac{1}{12\Delta^5}\sum_{m=0}^{\infty}\left(-\frac{1}{\Delta}\right)^m \frac{1}{(-2J/\Delta)^4} \tag{A1}$$

$$\times\left\{\frac{\langle D^3 I^m U^3\rangle_R}{3^m} + 3\langle D^2 U I^m D U^2\rangle_R\right.$$

$$+\frac{4(J/\Delta)}{(1-3J/\Delta)}\left[\frac{\langle D^3 I^m U U_1 U_{1'}\rangle_R}{3^m} + 3\langle D^2 U I^m D U_1 U_{1'}\rangle_R\right]$$

$$+\frac{4(J/\Delta)^2}{(1-4J/\Delta)(1-3J/\Delta)}\left[\frac{\langle D^3 I^m U U_{12'} U_{1'2}\rangle_R}{3^m}\right.$$

$$\left.+ 3\langle D^2 U I^m D U_{12'} U_{1'2}\rangle_R\right]$$

$$+\frac{4(J/\Delta)^2}{(1-3J/\Delta)^2}\left[\frac{\langle D_7 D_{7'} D I^m U U_1 U_{1'}\rangle_R}{3^m} + 3\langle D_7 D_{7'} U I^m D U_1 U_{1'}\rangle_R\right]$$

$$+\frac{8(J/\Delta)^3}{(1-4J/\Delta)(1-3J/\Delta)^2}\left[\frac{\langle D_7 D_{7'} D I^m U U_{12'} U_{1'2}\rangle_R}{3^m}\right.$$

$$\left.+ 3\langle D_7 D_{7'} U I^m D U_{12'} U_{1'2}\rangle_R\right]$$

$$+\frac{4(J/\Delta)^4}{(1-4J/\Delta)^2(1-3J/\Delta)^2}\left[\frac{\langle D_{78'} D_{7'8} I^m U U_{12'} U_{1'2}\rangle_R}{3^m}\right.$$

$$\left.\left.+ 3\langle D_{78'} D_{7'8} U I^m D U_{12'} U_{1'2}\rangle_R\right]\right\}.$$

Here we have subscripted the D operators with the subscripts 77' and 88'. These have an entirely equivalent meaning with respect to the D operators as the 11' and

22' subscripts have with respect to the U operators. Subscripts utilizing the intermediate numbers 33' to 66' will be needed when the operator I^m is replaced.

In order to perform the sum over m, we need to know the effect of I^m on $U^3|0>$, $UU_1U_{1'}|0>$, $UU_{12'}U_{1'2}|0>$, and $DU^2|0>$, $DU_1U_{1'}>$, $DU_{12'}U_{1'2}|0>$. This is determined in a manner analogous to that used to determine the effect of the operator I^m on $U^2|0>$, that is, by applying successively higher powers of the operator I to each term. As we saw in the series of equations leading to Eq. (51), i.e., Eqs. (42) and (44), each application of the operator I serves to introduce new terms derived from the old by linking two operators with a new subscript, as in Eq. (42) and Eq. (44). When all operators have been linked with a subscript, e.g., $U_{12'}U_{1'2}|0>$, Eq. (45), the resulting completely linked function is an eigenfunction of I, and the production of new terms ceases upon further application of I. There are sixteen different operators which can be formed from the basic operator, U^3, by the linking process. We list them, utilizing an extension of the subscript notation begun when the different linked operators formed from U^2 were defined. For clarity, we follow the list with the explicit expression for some of these subscripted operators, the definition of the others following directly.

(A2a) U^3,

(A2b) $UU_1U_{1'}$,

(A2c) $UU_{12'}U_{1'2}$,

(A2d) $U_2U_1U_{1'2'}$,

(A2e) $U_{2'}U_{12}U_{1'}$,

(A2f) $U_2U_{12'}U_{1'}$,

(A2g) $U_3U_{12'3'}U_{1'2}$,

(A2h) $U_{3'}U_{12'3}U_{1'2}$,

(A2i) $U_{23'}U_{13}U_{1'2'}$,

(A2j) $U_{23'}U_{12'}U_{1'3}$,

(A2k) $U_{34'}U_{12'3'}U_{1'24}$,

(A2l) $U_{34}U_{12'3'}U_{1'24'}$,

(A2m) $U_{34'}U_{12'3'4}U_{1'2}$,

(A2n) $U_{3'4'}U_{12'3}U_{1'24}$,

(A2o) $U_{34'5'}U_{12'3'5}U_{1'24}$,

(A2p) $U_{34'5'6}U_{12'3'5}U_{1'246'}$.

The definitions of $UU_1U_{1'}$ and $UU_{12'}U_{1'2}$ being simple extensions of $U_1U_{1'}$ and $U_{12'}U_{1'2}$, whose definitions were given in Eqs. (43) and (45), respectively, we begin with the definition of $U_2U_1U_{1'2'}$.

$$U_2U_1U_{1'2'}|0\rangle = \left(\frac{2}{N}\right)^2 J^3(1-a)^3 \sum_{\alpha\beta\gamma\delta\epsilon} \gamma_\alpha \gamma_\beta \gamma_\gamma \gamma_\delta \gamma_\epsilon \tag{A3a}$$

$$\times\ (S^-_{\alpha_1+\epsilon_1})(S^+_{-\alpha_2})(S^-_{\beta_1+\delta_1})(S^+_{-\beta_2})(S^-_{\gamma_1})(S^+_{-\gamma_2-\delta_2-\epsilon_2})|0\rangle,$$

$$U_{2'}U_{12}U_{1'}|0\rangle = \left(\frac{2}{N}\right)^2 J^3(1-a)^3 \sum_{\alpha\beta\gamma\delta\epsilon} \gamma_\alpha\gamma_\beta\gamma_\gamma\gamma_\delta\gamma_\epsilon \tag{A3b}$$

$$\times\ (S^-_{\alpha_1})(S^+_{-\alpha_2-\epsilon_2})(S^-_{\beta_1+\delta_1+\epsilon_1})(S^+_{-\beta_2})(S^-_{\gamma_1})(S^+_{-\gamma_2-\delta_2})|0\rangle,$$

$$U_2U_{12'}U_{1'}|0\rangle = \left(\frac{2}{N}\right)^2 J^3(1-a)^3 \sum_{\alpha\beta\gamma\delta\epsilon} \gamma_\alpha\gamma_\beta\gamma_\gamma\gamma_\delta\gamma_\epsilon \tag{A3c}$$

$$\times\ (S^-_{\alpha_1+\epsilon_1})(S^+_{-\alpha_2})(S^-_{\beta_1+\delta_1})(S^+_{-\beta_2-\epsilon_2})(S^-_{\gamma_1})(S^+_{-\gamma_2-\delta_2})|0\rangle,$$

$$U_3U_{12'3'}U_{1'2}|0\rangle = \left(\frac{2}{N}\right)^3 J^3(1-a)^3 \sum_{\alpha\beta\gamma\delta\epsilon\mu} \gamma_\alpha\gamma_\beta\gamma_\gamma\gamma_\delta\gamma_\epsilon\gamma_\mu \tag{A3d}$$

$$\times\ (S^-_{\alpha_1+\mu_1})(S^+_{-\alpha_2})(S^-_{\beta_1+\delta_1})(S^+_{-\beta_2-\epsilon_2-\mu_2})(S^-_{\gamma_1+\epsilon_1})(S^+_{-\gamma_2-\delta_2})|0\rangle,$$

$$U_{34'5'6}U_{12'3'5}U_{1'246'}|0\rangle = \left(\frac{2}{N}\right)^6 J^3(1-a)^3 \sum_{\alpha\beta\gamma\delta\epsilon\mu\nu\omega\sigma} \gamma_\alpha\gamma_\beta\gamma_\gamma\gamma_\delta\gamma_\epsilon\gamma_\mu\gamma_\nu\gamma_\omega\gamma_\sigma \tag{A3e}$$

$$\times\ (S^-_{\alpha_1+\mu_1+\sigma_1})(S^+_{-\alpha_2-\nu_2-\omega_2})(S^-_{\beta_1+\delta_1+\omega_1})(S^+_{-\beta_2-\epsilon_2-\mu_2})$$

$$\times\ (S^-_{\gamma_1+\epsilon_1+\nu_1})(S^+_{-\gamma_2-\delta_2-\sigma_2})|0\rangle.$$

We are now in a position to express the application of I^m to $U^3|0\rangle$, $UU_1U_{1'}|0\rangle$, and $UU_{12'}U_{1'2}|0\rangle$, in terms of a linear combination of functions made up from the operation of Eqs. (A2) to the Neel state. By successive application

of the operator I, we determine that,

$$
\begin{aligned}
I^m U^3|0\rangle = (-2J)^m \Big\{ & 3^m U^3|0\rangle + 6(4^m-3^m) U U_1 U_{1'}|0\rangle \qquad \text{(A4)} \\
& + 3(5^m-2.4^m+3^m)(U U_{12'} U_{1'2}|0\rangle + U_2 U_1 U_{1'2'}|0\rangle \\
& \quad + U_{2'} U_{12} U_{1'}|0\rangle + 2U_2 U_{12'} U_{1'}|0\rangle) \\
& + 2(6^m-3.5^m+3.4^m-3^m)(3U_3 U_{12'3'} U_{1'2}|0\rangle \\
& \quad + 3U_{3'} U_{12'3} U_{1'2}|0\rangle + 3U_{23'} U_{13} U_{1'2'}|0\rangle + U_{23'} U_{12'} U_{1'3}|0\rangle) \\
& + 3(7^m-4.6^m+6.5^m-4.4^m+3^m) \times (2U_{34'} U_{12'3'} U_{1'24}|0\rangle \\
& \quad + U_{34} U_{12'3'} U_{1'24'}|0\rangle + U_{34'} U_{12'3'4} U_{1'2}|0\rangle \\
& \quad + U_{3'4'} U_{12'3} U_{1'24}|0\rangle) \\
& + 6(8^m-5.7^m+10.6^m-10.5^m+5.4^m-3^m) \\
& \quad \times (U_{34'5'} U_{12'3'5} U_{1'24}|0\rangle) \\
& + (9^m-6.8^m+15.7^m-20.6^m+15.5^m-6.4^m+3^m) \\
& \quad \times (U_{34'5'6} U_{12'3'5} U_{1'246'}|0\rangle) \Big\},
\end{aligned}
$$

and for the operation of I^m onto $U U_1 U_{1'}|0\rangle$, we determine that

$$
\begin{aligned}
I^m U U_1 U_{1'}|0\rangle = (-2J)^m \Big\{ & 4^m U U_1 U_{1'}|0\rangle \qquad \text{(A5)} \\
& + (5^m-4^m)(U U_{12'} U_{1'2}|0\rangle + U_2 U_1 U_{1'2'}|0\rangle
\end{aligned}
$$

$$+U_{2'}U_{12}U_{1'}|0\rangle+2U_2U_{12'}U_{1'}|0\rangle)$$

$$+ (6^m-2.5^m+4^m)(3U_3U_{12'3'}U_{1'2}|0\rangle+3U_{3'}U_{12'3}U_{1'2}|0\rangle$$

$$+3U_{23'}U_{13}U_{1'2'}|0\rangle+U_{23'}U_{12'}U_{1'3}|0\rangle)$$

$$+ 2(7^m-3.6^m+3.5^m-4^m)(2U_{34'}U_{12'3'}U_{1'24}|0\rangle$$

$$+U_{34}U_{12'3'}U_{1'24'}|0\rangle+U_{34'}U_{12'3'4}U_{1'2}|0\rangle$$

$$+U_{3'4}U_{12'3}U_{1'24}|0\rangle)$$

$$+ 5(8^m-4.7^m+6.6^m-4.5^m+4^m)U_{34'5'}U_{12'3'5}U_{1'24}|0\rangle$$

$$+ (9^m-5.8^m+10.7^m-10.6^m+5.5^m-4^m)$$

$$\times (U_{34'5'6}U_{12'3'5}U_{1'246'}|0\rangle)\Big\}.$$

Finally, for the operation of I^m to $UU_{12'}U_{1'2}|0\rangle$, we get

$$I^m UU_{12'}U_{1'2}|0\rangle = (-2J)^m\Big\{5^m UU_{12'}U1'2|0\rangle \tag{A6}$$

$$+ 2(6^m-5^m)(U_3U_{12'3}U_{1'2}|0\rangle+U_{3'}U_{12'3}U_{1'2}|0\rangle)$$

$$+ (7^m-2.6^m+5^m)(2U_{34'}U_{12'3'}U_{1'24}|0\rangle$$

$$+U_{34}U_{12'2'}U_{1'24'}|0\rangle+2U_{34'}U_{12'3'4}U_{1'2}|0\rangle$$

$$+U_{3'4}U_{12'3}U_{1'24}|0\rangle)$$

$$+ 4(8^m-3.7^m+3.6^m-5^m)U_{34'5'}U_{12'3'5}U_{1'24}|0\rangle$$

$$+ (9^m-4.8^m+6.7^m-4.6^m+5^m)U_{34'5'6}U_{12'3'5}U_{1'246'}|0\rangle\Big\}.$$

For the successive application of I to the functions $DU^2|0\rangle$, $DU_1U_{1'}|0\rangle$, and $EU_{12'}U_{1'2}|0\rangle$, we cannot use the definition of I given in Eq. (20), Chapter III, since it was defined only in terms of its application to U-like operators. If, however, we first commute the D operator through all U-like operators until it operates on the Neel state, we are left with functions which involve only U-like operators, i.e.,

$$I^m DU^2|0\rangle = I^m[2\langle Q\rangle U|0\rangle + R|0\rangle] \tag{A7}$$

$$= 2\langle Q\rangle U|0\rangle + R|0\rangle;\ m = 0$$

$$= (-2J)^m[2\langle Q\rangle U|0\rangle + R'|0\rangle];\ m \neq 0$$

where

$$R'|0\rangle = \left(\tfrac{2}{N}\right)J^3(1-a)^3 \sum_{\alpha'\alpha\beta} \gamma_{\alpha'}\gamma_\alpha\gamma_\beta \tag{A8}$$

$$\times\ [-8\left(\tfrac{N}{2}\right)^{-1} \sum_{\gamma} \gamma_\gamma (S^-_{\alpha_1+\gamma_1})(S^z_{\alpha_1'+\beta_1})(S^+_{-\beta_2-\gamma_2})(S^z_{-\alpha_2'-\alpha_2})$$

$$- 2(S^-_{\alpha_1'+\alpha_1+\beta_1})(S^+_{-\alpha_2})(S^+_{-\beta_2})(S^-_{-\alpha_2'})$$

$$+ 2(S^-_{\alpha_1})(S^-_{\beta_1})(S^+_{-\alpha_2'})(S^+_{-\alpha_2'-\alpha_2-\beta_2})$$

$$+ 8\left(\tfrac{N}{2}\right)^{-1/2}(S^-_{\alpha_1'+\alpha_1+\beta_1})(S^+_{-\alpha_2})(S^z_{-\alpha_2'-\beta_2})$$

$$- 8\left(\tfrac{N}{2}\right)^{-1/2}(S^-_{\alpha_1})(S^z_{\alpha_1'+\beta_1})(S^+_{-\alpha_2'-\alpha_2-\beta_2})$$

$$+ 4(\tfrac{N}{2})^{-1}(S^{-}_{\alpha_1'+\alpha_1+\beta_1})(S^{+}_{-\alpha_2'-\alpha_2-\beta_2})].$$

In order to simplify the expression of the results which follow, we introduce the following abbreviation,

$$DU^2|0\rangle^{(1)} = [2\langle Q\rangle U|0\rangle + R'|0\rangle]. \qquad (A9)$$

For successive applications of I to $DU_1U_{1'}|0\rangle$, we get

$$I^m DU_1U_{1'}|0\rangle = I^m[2(\tfrac{2}{N})\gamma_0\langle Q\rangle U|0\rangle + R_{11'}|0\rangle] \qquad (A10)$$

$$= DU_1U_{1'}|0\rangle;\ m = 0$$

$$= (-2J)^m DU_1U_{1'}|0\rangle^{(1)};\ m \neq 0$$

Since all U-like operators are maximally connected in $DU_{12'}U_{1'2}|0\rangle$, we get

$$I^m DU_{12'}U_{1'2}|0\rangle = (-2J)^m DU_{12'}U_{1'2}|0\rangle. \qquad (A11)$$

The insertion of Eqs. (A4)-(A7), and Eqs. (A10)-(A11) into Eq. (A1), with the subsequent summation over the index m, results in the sixth order analog of the fourth order expression given in Eq. (52), Chapter III. Thus we have completed the first phase of the Appendix.

The second phase consists of determining the explicit sixth order energy correction to the linear chain coupled

spin one-half. The first step in this operation is to write out the results of the summation over the index m for those matrix elements which contribute to this case. If, after the summation over the index m, a matrix element has a coefficient involving the factor $(1-4J/\Delta)^{-1}$, then the corresponding matrix element must be null for the case of the linear chain with spin one-half. If this were not the case, then the perturbation series would diverge, since $(1-4J/\Delta) = 0$ for this case. We prove this for two matrix elements in Appendix B, and assume it for the rest. The summation over the index m for the terms contributing to the sixth order energy correction under the above assumption thus yields

$$E^{(1-a)^6}_{S=1/2,\gamma_0=2} = -\frac{1}{12\Delta^5}\left\{\frac{\langle D^3U^3\rangle_R}{(1-2/J\Delta)^5} + \frac{4(J/\Delta)(2-5J/\Delta)\langle D^3UU_1U_{1'}\rangle_R}{(1-3J/\Delta)(1-8J/3\Delta)(1-2J/\Delta)^5}\right. \tag{A12}$$

$$+ \frac{8/3(J\Delta)^2(2-5J/\Delta)[\langle D^3U_2U_1U_{1'2'}\rangle_R + \langle D^3U_{2'}U_{12}U_{1'}\rangle_R + 2\langle D^3U_2U_{12'}U_{1'}\rangle_R\rangle}{(1-10J/3\Delta)(1-3J/\Delta)(1-8J/\Delta)(1-2J/\Delta)^5}$$

$$+ \frac{4(J/\Delta)^2\langle D_7D_{7'}DUU_1U_{1'}\rangle_R}{(1-3J/\Delta)^2(1-8J/3\Delta)(1-2J/\Delta)^4}$$

$$+ \frac{8/3(J/\Delta)^3[\langle D_7D_{7'}DU_2U_1U_{1'2'}\rangle_R + \langle D_7D_{7'}DU_{2'}U_{12}U_{1'}\rangle_R + 2\langle D_7D_{7'}DU_2U_{12'}U_{1'}\rangle_R}{(1-10J/3\Delta)(1-3J/\Delta)^2(1-8J/3\Delta)(1-2J/\Delta)^4}\Bigg\}$$

$$- \frac{1}{4\Delta^5}\Bigg\{\frac{\langle D^2UDU^2\rangle_R}{(1-2J/\Delta)^4} + \frac{2(J/\Delta)\langle D^2UDU^2\rangle_R^{(1)}}{(1-2J/\Delta)^5}$$

$$+ \frac{4(J/\Delta)\langle D^2UDU_1U_{1'}\rangle_R}{(1-3J/\Delta)(1-2J/\Delta)^4} + \frac{8(J/\Delta)^2\langle D^2UDU_1U_{1'}\rangle_R^{(1)}}{(1-3J/\Delta)(1-2J/\Delta)^5}$$

$$+ \frac{4(J/\Delta)^2\langle D_7D_{7'}UDU_1U_{1'}\rangle_R}{(1-3J/\Delta)^2(1-2J/\Delta)^4} + \frac{8(J/\Delta)^3\langle D_7D_{7'}UDU_1U_{1'}\rangle_R^{(1)}}{(1-3J/\Delta)^2(1-2J/\Delta)^5}\Bigg\}.$$

There are apparently fifteen matrix elements to compute in Eq. (A12). We can use the Hermitian property of the matrix elements to reduce the number of elements, since they are not linearly independent. Using the relationship $\langle 0|D^3I - (IU^3|0\rangle)^+$, along with Eq. (A4) with m = 1 and Eq. (A5) with m = 1, we obtain

$$\begin{aligned}\langle D^3IUU_1U_{1'}\rangle_R &= (-2J)\Big\{3\langle D^3UU_1U_{1'}\rangle_R + 6\langle D_7D_{7'}DUU_1U_{1'}\rangle_R\Big\} \\ &= (-2J)\Big\{4\langle D^3UU_1U_{1'}\rangle_R + \langle D^3UU_{12'}U_{1'2}\rangle_R \\ &\quad + \langle D^3U_2U_1U_{1'2'}\rangle_R + \langle D^3U_{2'}U_{12}U_{1'}\rangle_R \\ &\quad + 2\langle D^3U_2U_{1'2'}U_{1'}\rangle_R\Big\}.\end{aligned} \tag{A13}$$

For $S = 1/2$, $\gamma_0 = 2$, Eq. (A13) yields

$$\begin{aligned}&\langle D^3U_2U_1U_{1'2'}\rangle_R + \langle D^3U_{2'}U_{12}U_{1'}\rangle_R + 2\langle D^3U_2U_{1'2'}U_{1'}\rangle_R \\ &\quad = 6\langle D_7D_{7'}DUU_1U_{1'}\rangle_R - \langle D^3UU_1U_{1'}\rangle_R,\end{aligned} \tag{A14}$$

since $\langle D^3UU_{12'}U_{1'2}\rangle_R = 0$ for this case. This is one of the matrix elements which we show explicitly to be null in Appendix B.

Using the same Hermitian property and a combination of Eqs. (A4)-(A6), we obtain the following two equalities,

$$\begin{aligned}&\langle D^3IU_2U_1U_{1'2'}\rangle_R + \langle D^3IU_{2'}U_{12}U_{1'}\rangle_R + 2\langle D^3IU_2U_{12'}U_{1'}\rangle_R \\ &\quad = (-2J)\Big\{5[\langle D^3U_2U_1U_{1'2'}\rangle_R + \langle D^3U_{2'}U_{12}U_{1'}\rangle_R \\ &\quad + 2\langle D^3U_2U_{12'}U_{1'}\rangle_R] \\ &\quad + 2[2\langle D^3U_3U_{12'3'}U_{1'2}\rangle_R + 2\langle D^3U_{3'}U_{12'3}U_{1'2}\rangle_R \\ &\quad + 3\langle D^3U_{23'}U_{13}U_{1'2'}\rangle_R + \langle D^3U_{23'}U_{12'}U_{1'3}\rangle_R]\Big\} \\ &\quad = (-2J)\Big\{3[\rangle D^3U_2U_1U_{1'2'}\rangle_R + \langle D^3U_{2'}U_{12}U_{1'}\rangle_R \\ &\quad + 2\langle D^3U_2U_{12'}U_{1'}\rangle_R] \\ &\quad + 6[\langle D_7D_{7'}DU_2U_1U_{1'2'}\rangle + \langle D_7D_{7'}DU_{2'}U_{12}U_{1'}\rangle_R \\ &\quad + 2\langle D_7D_{7'}DU_2U_{12'}U_{1'}\rangle\ ]\Big\}.\end{aligned} \tag{A15}$$

Since for the case of the linear chain with spin one-half we have assumed the following null relationship,

$$2\langle D^3U_3U_{12'3'}U_{1'2}\rangle_R + 2\langle D^3U_{3'}U_{12'3}U_{1'2}\rangle_R \qquad \text{(A16)}$$
$$+ 3\langle D^3U_{23'}U_{13}U_{1'2'}\rangle_R + \langle D^3U_{23'}U_{12'}U_{1'3}\rangle_R = 0,$$

we obtain for this case,

$$\langle D_7D_{7'}DU_2U_1U_{1'2'}\rangle_R + \langle D_7D_{7'}DU_{2'}U_{12}U_{1'}\rangle_R \qquad \text{(A17)}$$
$$+ 2\langle D_7D_{7'}DU_2U_{12'}U_{1'}\rangle_R = 1/3$$
$$= 1/3[\ \langle D^3U_2U_{1'}U_{12'}\rangle_R + \langle D^3U_{2'}U_{12}U_{1'}\rangle_R$$
$$+ 2\langle D^3U_2U_{12'}U_{1'}\rangle_R].$$

With the reationships Eq. (A14) and Eq. (A17), the number of independent matrix elements is reduced to nine for Eq. (A12).

The first step in the calculation of these nine matrix elements is to commute each D-like operator through all U-like operators until it operates upon the Neel state. The results are then given in terms of the commutators between D and U as defined in Chapter III, Section A, Part 2. It should be remembered that the subscript R on the matrix elements indicates that all terms proportional to powers of N greater than one are to be disregarded, as shown in

Chapter III, Section A, Part 2. Thus we get for the nine matrix elements of interest,

$$\langle D^3U^3\rangle_R = 2\langle R^+R\rangle + \langle V\rangle, \tag{A18a}$$

$$\langle D^3UU_1U_{1'}\rangle = 6(\tfrac{2}{N})\gamma_0\langle F\rangle\langle Q\rangle + \langle R^+R_{11'}\rangle + \langle R_1^+R_{1'}\rangle + \langle V_{11'}\rangle, \tag{A18b}$$

$$\begin{aligned}\langle D_7D_{7'}DUU_1U_{1'}\rangle_R &= 4(\tfrac{2}{N})\gamma_0\langle F\rangle\langle Q\rangle + 2\langle F_{17}\rangle\langle Q_{1'7'}\rangle \\ &+ 2\langle F_{1'7}\rangle\langle Q_{17'}\rangle + 4(\tfrac{2}{N})^2\gamma_0{}^2\langle Q\rangle^3 \\ &+ \langle R^+_{77'}R_{11'}\rangle + \langle R^+_{177'}R_{1'}\rangle + \langle V_{11'77'}\rangle,\end{aligned} \tag{A18c}$$

$$\langle D^2UDU^2\rangle_R = \langle R^+R\rangle, \tag{A18d}$$

$$\langle D^2UDU_1U_{1'}\rangle_R = 2(\tfrac{2}{N})\gamma_0\langle F\rangle\langle Q\rangle + \langle R^+R_{11'}\rangle, \tag{A18e}$$

$$\langle D_7D_{7'}UDU_1U_{1'}\rangle_R = 4(\tfrac{2}{N})\gamma_0\langle F\rangle\langle Q\rangle + 4(\tfrac{2}{N})^2\gamma_0^2\langle Q\rangle^3 + \langle R^+_{77'}R_{11'}\rangle, \tag{A18f}$$

$$\langle D^2UDU^2\rangle_R^{(1)} = \langle R^+R^-\rangle, \tag{A18g}$$

$$\langle D^2UDU_1U_{1'}\rangle^{(1)} = 2(\tfrac{2}{N})\gamma_0\langle F\rangle\langle Q\rangle + \langle R^+R^-\rangle, \tag{A18h}$$

$$\langle D_7D_{7'}UDU_1U_{1'}\rangle_R^{(1)} = 4(\tfrac{2}{N})\gamma_0\langle Q\rangle\langle F\rangle + 4(\tfrac{2}{N})^2\gamma_0^2\langle Q\rangle + \langle R^+_{77'}R'\rangle. \tag{A18i}$$

To complete the evaluation of these matrix elements, the commutators of Eqns. (18a-i) are replaced by their expressions in terms of spin operators, being careful to observe the linking of operators indicated by the subscripts. The resulting general expressions are then,

$$\langle D^3U^3\rangle_R = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6 \times \Big\{12(S\gamma_0)^6\,\frac{(15\gamma_0^{\,2}-45\gamma_0+40)}{\gamma_0^{\,4}} \tag{A19a}$$

$$- 216(S\gamma_0)^5\,\frac{\gamma_0-1}{\gamma_0^{\,2}} + 24(S\gamma_0)^4\,\frac{(3\gamma_0^{\,2}+2\gamma_0-2)}{\gamma_0^{\,2}}$$

$$- 54(S\gamma_0) + 9\Big\},$$

$$\langle D^3UU_1U_{1'}\rangle_R = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6 \times \Big\{6(S\gamma_0)^6 \tag{A19b}$$

$$\times\ 6(S\gamma_0)^6\left[\frac{6\gamma_0^{\,3}+18\gamma_0^{\,2}-63\gamma_0+49}{\gamma_0^{\,4}}\right]$$

$$- 12(S\gamma_0)^5\left[\frac{2\gamma_0^{\,3}+16\gamma_0^{\,2}-11\gamma_0^{\,-7}}{\gamma_0^{\,3}}\right]$$

$$+ 6(S\gamma_0)^4\left[\frac{12\gamma_0^{\,2}+21\gamma_0-21}{\gamma_0^{\,2}}\right] - 54(S\gamma_0)^3 + 9(S\gamma_0)^2\ ,$$

$$\langle D_7D_{7'}DUU_1U_{1'}\rangle_R = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6 \tag{19c}$$

To complete the evaluation of these matrix elements, the commutators of Eqns. (18a-i) are replaced by their expressions in terms of spin operators, being careful to observe the linking of operators indicated by the subscripts. The resulting general expressions are then,

$$\langle D^3U^3\rangle_R = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6 \times \Big\{12(S\gamma_0)^6\,\frac{(15\gamma_0^{\,2}-45\gamma_0+40)}{\gamma_0^{\,4}} \tag{A19a}$$

$$- 216(S\gamma_0)^5\,\frac{\gamma_0-1}{\gamma_0^{\,2}} + 24(S\gamma_0)^4\,\frac{(3\gamma_0^{\,2}+2\gamma_0-2)}{\gamma_0^{\,2}}$$

$$- 54(S\gamma_0) + 9\Big\},$$

$$\langle D^3UU_1U_{1'}\rangle_R = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6 \times \Big\{6(S\gamma_0)^6 \tag{A19b}$$

$$\times\ 6(S\gamma_0)^6\left[\frac{6\gamma_0^{\,3}+18\gamma_0^{\,2}-63\gamma_0+49}{\gamma_0^{\,4}}\right]$$

$$- 12(S\gamma_0)^5\left[\frac{2\gamma_0^{\,3}+16\gamma_0^{\,2}-11\gamma_0-7}{\gamma_0^{\,3}}\right]$$

$$+ 6(S\gamma_0)^4\left[\frac{12\gamma_0^{\,2}+21\gamma_0-21}{\gamma_0^{\,2}}\right] - 54(S\gamma_0)^3 + 9(S\gamma_0)^2\ ,$$

$$\langle D_7D_{7'}DUU_1U_{1'}\rangle_R = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6 \tag{19c}$$

$$x\left\{+(S\gamma_0)^6\,\frac{4\gamma_0^4+32\gamma_0^3+132\gamma_0^2-351\gamma_0+203}{\gamma_0^4}\right.$$

$$-2(S\gamma_0)^5\,\frac{11\gamma_0^3+101\gamma_0^2-46\gamma_0-77}{\gamma_0^3}$$

$$\left.+(S\gamma_0)^4\,\frac{67\gamma_0^2+147\gamma_0-147}{\gamma_0^2}-54(S\gamma_0)^3+9(S\gamma_0)^2\right\},$$

$$\langle D^2UDU^2\rangle_R=\frac{J^6(1-a)^6}{\gamma_0^2}\left(\frac{N\gamma_0}{2}\right)2^6(S\gamma_0)^2 \tag{A19d}$$

$$x\left\{4(S\gamma_0)^4\,\frac{(15\gamma_0^2-45\gamma_0+40)}{\gamma_0^4}-48(S\gamma_0)^3\,\frac{\gamma_0-1}{\gamma_0^2}\right.$$

$$\left.+4(S\gamma_0)^2\,\frac{(4\gamma_0^2+3\gamma_0-3)}{\gamma_0^2}-8(S\gamma_0)+1\right\},$$

$$\langle D^2UDU_1U_{1'}\rangle_R=\frac{J^6(1-a)^6}{\gamma_0^2}\left(\frac{N\gamma_0}{2}\right)2^6 \tag{A19e}$$

$$x\left\{2(S\gamma_0)^6\,\frac{6\gamma_0^3+18\gamma_0^2-63\gamma_0+49}{\gamma_0^4}\right.$$

$$-8(S\gamma_0)^5\,\frac{\gamma_0^2+6\gamma_0-6}{\gamma_0^2}+6(S\gamma_0)^4\,\frac{3\gamma_0^2+2\gamma_0-2}{\gamma_0^2}$$

$$\left.-8(S\gamma_0)^3+(S\gamma_0)^2\right\},$$

$$\langle D_7 D_{7'} U D U_1 U_{1'} \rangle_R = \frac{J^6 (1-a)^6}{\gamma_0^{\,2}} \left(\frac{N\gamma_0}{2}\right) 2^6 \tag{A19f}$$

$$\times \left\{ (S\gamma_0)^6 \frac{4\gamma_0^{\,4} + 24\gamma_0^{\,3} + 18\gamma_0^{\,2} - 99\gamma_0 + 67}{\gamma_0^{\,4}} \right.$$

$$- 16(S\gamma_0)^5 \frac{\gamma_0^{\,2} + 3\gamma_0 - 3}{\gamma_0^{\,2}} + 4(S\gamma_0)^4 \frac{5\gamma_0^{\,2} + 3\gamma_0 - 3}{\gamma_0^{\,2}}$$

$$\left. - 8\,(S\gamma_0)^3 + (S\gamma_0)^2 \right\},$$

$$\langle D^2 U D U^2 \rangle_R^{(1)} = \frac{J^6 (1-a)^6}{\gamma_0^{\,2}} \left(\frac{N\gamma_0}{2}\right) 2^6 \tag{A19g}$$

$$\times \left\{ 36(S\gamma_0)^6 \frac{(\gamma_0 - 1)^2}{\gamma_0^{\,4}} - 48(S\gamma_0)^5 \frac{\gamma_0 - 1}{\gamma_0^{\,2}} \right.$$

$$\left. + 4(S\gamma_0)^4 \frac{4\gamma_0^{\,2} + 3\gamma_0 - 3}{\gamma_0^{\,2}} - 8(S\gamma_0)^3 + (S\gamma_0)^2 \right\},$$

$$\langle D^2 U D U_1 U_{1'} \rangle_R^{(1)} = \frac{J^6 (1-a)^6}{\gamma_0^{\,2}} \left(\frac{N\gamma_0}{2}\right) 2^6 \tag{A19h}$$

$$\times \left\{ 12(S\gamma_0)^6 \frac{\gamma_0^{\,3} + 2\gamma_0^{\,2} - 6\gamma_0 + 3}{\gamma_0^{\,4}} \right.$$

$$- 8(S\gamma_0)^5 \frac{\gamma_0^{\,2} + 6\gamma_0 - 6}{\gamma_0^{\,2}} + 6(S\gamma_0)^4 \frac{3\gamma_0^{\,2} + 2\gamma_0 - 2}{\gamma_0^{\,2}}$$

$$- 8(S\gamma_0)^3 + (S\gamma_0)^2\Big\}.$$

$$\langle D_7 D_{7'} UDU_1 U_{1'}\rangle_R^{(1)} = \frac{J^6(1-a)^6}{\gamma_0^2}\left(\frac{N\gamma_0}{2}\right)2^6 \tag{A19i}$$

$$\times\Big\{4(S\gamma_0)^6 \frac{\gamma_0^4 + 6\gamma_0^3 + 3\gamma_0^2 - 18\gamma_0 + 9}{\gamma_0^4}$$

$$- 16(S\gamma_0)^5 \frac{\gamma_0^2 + 3\gamma_0 - 3}{\gamma_0^2} + 4(S\gamma_0)^4 \frac{5\gamma_0^2 + 3\gamma_0 - 3}{\gamma_0^2}$$

$$- 8(S\gamma_0)^3 + (S\gamma_0)^2\Big\}.$$

Putting $S = 1/2$ and $\gamma_0 = 2$ into Eqs. (A19a-i) and using Eqs. (A14) and (A17), provides numerical values for all necessary matrix elements in the calculation of the sixth order energy correction for the linear chain with spin one-half. Substitution into Eq. (A12) yields $E^{(1-a)^6}_{S=1/2,\gamma_0=2} = 0$, in agreement with Walker.[19]

APPENDIX B

In this Appendix, we show explicitly that, for the linear chain with spin one-half,

$$\langle D^3 U U_{12'} U_{1'2} \rangle_R = 0, \tag{B1}$$

and

$$\langle D^2 U D U_{12'} U_{1'2} \rangle_R = 0 \tag{B2}$$

Eqs. (B1) and (B2) represent typical terms resulting from Eq. (53), Chapter III, which have denominators which vanish for this case. It should be realized that the vanishing of the denominators, coupled with the vanishing of the matrix elements, does not indicate an indeterminacy in the evaluation of the corresponding term in Eq. (53). In the course of computing succeeding orders of the perturbation correction, matrix elements like Eqs. (B1) and (B2) appear with finite coefficients early in the series. It is at this point that their null property should be taken into account, and not after the sum of all possible coefficients throughout the perturbation series has been determined for a given matrix element under the assumption that it is not null.

We consider first the form of $\langle D^3 UU_{12'}U_{1'2}\rangle_R$.

$$\langle D^3 UU_{12'}U_{1'2}\rangle_R = 6\langle Q_{12'}\rangle\langle r^-_{1'2}\rangle + \langle R^+ R_{11'22'}\rangle \tag{B3}$$

$$+ \langle R^+_{12'} R_{1'2}\rangle + \langle V_{11'22'}\rangle,$$

which is determined by means of the commutators of D and U defined in Chapter III, Section A, Part 2. The subscripts refer to the linking of operators discussed in Appendix A. Substitution of the commutators with their expressions in terms of spin operators, and the subsequent evaluation of these expressions, yields

$$\langle D^3 UU_{12'}U_{1'2}\rangle_R = \frac{J^6(1-a)^6}{\gamma_0^{\,2}} \left(\frac{N\gamma_0}{2}\right)2^6 \tag{B4}$$

$$\times\left\{216(S\gamma_0)^6 \frac{(\gamma_0-1)^2}{\gamma_0^{\,4}} - 24(S\gamma_0)^5 \frac{10\gamma_0^{\,2} - 5\gamma_0 - 7}{\gamma_0^{\,3}}\right.$$

$$\left. + 6(S\gamma_0)^4 \frac{10\gamma_0^{\,2} + 27\gamma_0 - 27}{\gamma_0^{\,2}} - 54(S\gamma_0)^3 + 9(S\gamma_0)^2\right\}$$

which for $S = 1/2$, $\gamma_0 = 2$, gives

$$\langle D^3 UU_{12'}U_{1'2}\rangle_R = 0 \tag{B5}$$

For the form of $\langle D^2UDU_{12'}U_{1'2}\rangle_R$, we find upon applying the commutation relations between D and U,

$$\langle D^2UDU_{12'}U_{1'2}\rangle_R = 2\langle Q_{12'}\rangle\langle Q_{1'2}\rangle + \langle R^+R_{11'22'}\rangle, \quad \text{(B6)}$$

which, upon replacement of the commutators with their equivalents in terms of spin operators and subsequent evaluation thereof, yields

$$\langle D^2UDU_{12'}U_{1'2}\rangle_R = \frac{J^6(1-a)^6}{\gamma_0^{\,2}}\left(\frac{N\gamma_0}{2}\right)2^6 \quad \text{(B7)}$$

$$\times\left\{72(S\gamma_0)^6\,\frac{(\gamma_0-1)^2}{\gamma_0^{\,4}} - 72(S\gamma_0)^5\,\frac{(\gamma_1-1)}{\gamma_0^{\,2}}\right.$$

$$\left. + (S\gamma_0)^4\,\frac{16\gamma_0^{\,2}+18\gamma_0-18}{\gamma_0^{\,2}} - 8(S\gamma_0)^3 + (S\gamma_0)^2\right\}.$$

Substitution of $S = 1/2$, $\gamma_0 = 2$ into Eq. (B7) then yields the predicted result,

$$\langle D^2UDU_{12'}U_{1'2}\rangle_R = 0. \quad \text{(B8)}$$

APPENDIX C

In this Appendix, we will compute the fourth order perturbation correction to the partition function as it is expressed in Eq. (103), Chapter IV. The computation is not carried out to the point of providing a numerical correction, expressed as a function of spin and lattice, but only so far as to show the validity of relationships such as Eq. (113) and Eq. (114) to fourth order. The fourth order perturbation correction is given by the non-vanishing elements of

$$\sum_{n=0}^{N} \sum_{n_1+n_2=n} \langle n, n_1 n_2 | \frac{1}{2\pi i} \oint \exp\,(-\beta E)\, dE \tag{C1}$$

$$\times \sum_{m=0}^{\infty} \left(\frac{1}{E - H_0} I\right)^m \frac{1}{E - H_0}(D+U) \sum_{n=0}^{\infty} \left(\frac{1}{E - H_0} I\right)^n \frac{1}{E - H_0}(D+U)$$

$$\times \sum_{p=0}^{\infty} \left(\frac{1}{E - H_0} I\right)^p \frac{1}{E - H_0}(D+U) \sum_{q=0}^{\infty} \left(\frac{1}{E - H_0} I\right)^q \frac{1}{E - H_0}(D+U)$$

$$\times \sum_{r=0}^{\infty} \left(\frac{1}{E - H_0} I\right)^r \frac{1}{E - H_0} | n, n_1 n_2 \rangle .$$

The non-vanishing elements of Eq. (C1) are, of course, those in which the number of D operators is equal to the

number of U operators. These terms correspond to the following ordering of the D and U operators,

$$\begin{aligned} &DUDU, \\ &UDUD, \\ &DUUD, \\ &UDDU, \\ &DDUU, \\ \text{and} \quad &UUDD. \end{aligned} \tag{C2}$$

Evaluation of the corresponding six integrals obtained from Eq. (C1), and an expansion of each in powers of exp $(-\beta\Delta/2)$, yields the following result for the sum of contributions from all six integrals, plus the zeroth and second order corrections of Eq. (110).

$$\begin{aligned} &\mathrm{Tr}[\exp(-\beta H)]_{\text{to fourth order}} \qquad (C3) \\ &= \exp(-\beta E_0)\Big\{1 + \langle 0|O_A|0\rangle + \sum_{n_1+n_2=2} \langle 2,n_1n_2|O_B|2,n_1n_2\rangle \\ &+ \sum_{n_1+n_2=4} \langle 4,n_1n_2|O_C|4,n_1n_2\rangle\Big\} \\ &+ \exp[-\beta(E_0+\Delta/2)\Big\{N + \sum_{n_1+n_2=1} \langle 1,n_1n_2|O_A|1,n_1n_2\rangle \\ &+ \sum_{n_1+n_2=3} \langle 3,n_1n_2|O_B|3,n_1n_2\rangle \\ &+ \sum_{n_1+n_2=5} \langle 5,n_1n_2|O_C|5,n_1n_2\rangle\Big\} + \ldots, \end{aligned}$$

where

$$O_A = [- D\frac{1}{(\Delta+I)^2}U + 2D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^3}U \tag{C4}$$

$$+ D\frac{1}{(\Delta+I)^2}UD\frac{1}{(\Delta+I)^2}U - D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)^2}U\frac{1}{(\Delta+I)}U$$

$$- 2D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)^2}U]$$

$$+\beta[D\frac{1}{(\Delta+I)}U - 2D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^2}U + D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)}U]$$

$$+ \beta^2/2[D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)}U],$$

$$O_B = [\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)} - 2\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^2} \tag{C5}$$

$$- \frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^2}UD\frac{1}{(\Delta+I)} + \frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)}$$

$$+ \frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)}] + \beta[\frac{1}{\Delta + I}UD\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)}],$$

$$O_C = \frac{1}{2\Delta + I}U\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}. \tag{C6}$$

The properties of the D and U operators allow the following relationships to be used to simplify Eq. (C3),

$$\sum_{n_1+n_2=2} \langle 2, n_1 n_2 | O_B | 2, n_1 n_2 \rangle = \langle 0 | O_B' | 0 \rangle, \tag{C7}$$

$$\sum_{n_1+n_2=4} \langle 4, n_1 n_2 | O_C | 4, n_1 n_2 \rangle = \langle 0 | O_C' | 0 \rangle, \tag{C8}$$

$$\sum_{n_1+n_2=3} \langle 3, n_1 n_2 | O_B | 3, n_1 n_2 \rangle = \sum_{n_1+n_2=1} \langle 1, n_1 n_2 | O_B' | 1, n_1 n_2 \rangle, \tag{C9}$$

$$\sum_{n_1+n_2=5} \langle 5, n_1 n_2 | O_C | 5, n_1 n_2 \rangle = \sum_{n_1+n_2=1} \langle 1, n_1 n_2 | O_C' | 1, n_1 n_2 \rangle, \tag{C10}$$

where

$$O_B' = D\frac{1}{(\Delta+I)^2}U - 2D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^3}U - D\frac{1}{(\Delta+I)^2}UD\frac{1}{(\Delta+I)^2}U \tag{C11}$$

$$+ 2D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)^2}U] + \beta[D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^2}U],$$

$$O_C' = D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)^2}U\frac{1}{(\Delta+I)}U. \tag{C12}$$

For the terms proportional to exp $(-\beta E_0)$, the simplified expression for the partition function to fourth order is

$$\exp(-\beta E_0)\Big\{1 + \beta[\langle 0| D\frac{1}{(\Delta+I)}U|0\rangle - \langle 0| D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^2}U|0\rangle \tag{C13}$$

$$+ \langle 0 | D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)}U | 0\rangle]$$

$$+ \beta^2/2[\langle 0 | D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)}U | 0\rangle]\Big\}.$$

We see that Eq. (C13) represents an expansion to fourth order, i.e., through all terms involving at least two D and two U operators, of the following exponential,

$$\langle 0 | \exp[-\beta(E_0 - D\frac{1}{(\Delta+I)}U + D\frac{1}{(\Delta+I)}UD\frac{}{(\Delta+I)^2}U \tag{C14}$$

$$- D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)}U + \ldots)]|0\rangle.$$

In addition, the expectation value of $-1/\beta$ times the argument forms precisely the same perturbation series for the ground state as was determined in Chapter III. This may be seen by simply utilizing the binomial theorem to obtain

$$\langle 0 | D\frac{1}{(\Delta+I)}U | 0\rangle = \frac{\langle DU\rangle}{\Delta} - \frac{\langle DIU\rangle}{\Delta^2} + \frac{\langle DI^2U\rangle}{\Delta^3} + \ldots, \tag{C15}$$

$$\langle 0 | D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^2}U | 0\rangle = \frac{\langle DU\rangle 2}{\Delta^3} \quad \frac{3\langle DU\rangle\langle DIU\rangle}{\Delta^4}$$

$$+ \frac{6\langle DU\rangle\langle DI^2U\rangle}{\Delta^5} - \ldots,$$

$$\langle 0| D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)}U|0\rangle = \frac{\langle D^2U^2\rangle}{2\Delta^3} - \frac{\langle D^2UIU\rangle}{\Delta^4} - \frac{\langle D^2IU^2\rangle}{4\Delta^4}$$

$$+ \frac{\langle D^2IUIU\rangle}{2\Delta^5} + \frac{\langle D^2I^2U^2\rangle}{8\Delta^5} + \frac{3\langle D^2IU^2U\rangle}{2\Delta^5} + \ldots$$

If Eq. (C15) is substituted into the argument of Eq. (C14), all the terms of the ground state perturbation series of Eq. (32), Chapter III, in which there are only two D and two U operators or less are accounted for. Thus Eq. (113), Chapter IV, is valid through the fourth order of the perturbation.

To show Eq. (114) through fourth order, we take the terms of Eq. (C3) which are proportional to $\exp[(-\beta(E_0+\Delta/2)]$, and introduce the simplifications indicated in Eqs. (C9-12). We get

$$\exp[-\beta(E_0+\Delta/2)]\Big\{N + \beta\sum_{n_1+n_2=1}\langle 1,n_1n_2| \tag{C16}$$

$$\times\ [D\frac{1}{(\Delta+I)}U - D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)^2}U$$

$$+ D\frac{1}{(\Delta+I)}D\frac{1}{(2\Delta+I)}U\frac{1}{(\Delta+I)}U]|1,n_1n_2\rangle$$

$$+ \beta^2/2\sum_{n_1+n_2=1}\langle 1,n_1n_2|[D\frac{1}{(\Delta+I)}UD\frac{1}{(\Delta+I)}U]|1,n_1n_2\rangle$$

Examination of Eq. (C16) shows that, to fourth order, it represents the expansion indicated in Eq. (114).

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